

A STUDY OF SOME CHLORONITROSO COMPOUNDS

with special reference to their suitability  
for asymmetric photolysis.

T H E S I S

submitted to the

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for the

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by

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INTRODUCTION: HISTORICAL and THEORETICAL

Optical Rotatory Power.

Fresnel has shown that when a beam of plane polarised light is transmitted through a transparent optically active medium it gives rise to two circularly polarised beams of opposite sense, possessing the same amplitude but travelling with different velocities. Thus optical rotatory power can be attributed to a difference in the refractive indices  $n_r$  and  $n_l$  for right and left handed circularly polarised light. As the plane polarised ray proceeds through the medium a phase difference between the two circular components is set up, which produces a rotation of the plane of polarisation of the resultant wave. In a path of one centimetre the plane of polarisation rotates through an angle  $\theta$ , given by  $\theta = \frac{\pi}{\lambda_0} (n_r - n_l)$  where  $\lambda_0$  is the wave length of light in vacuo.

The variation of  $\theta$  with the wave length of light employed is commonly known as rotatory dispersion. In an attempt to find a theoretical explanation of this dispersion, Drude<sup>2</sup> assumed that in a transparent optically active medium the electrons describe helical paths and finally arrived at the well known equation, 
$$\theta = \sum \frac{K}{\lambda^2 - \lambda_0^2}$$

This equation has frequently been used to express the rotatory dispersion of compounds in the region of transparency. For normal rotatory dispersion one term of the

equation is sufficient but for the 'anomalous' rotatory dispersion displayed by substances such as ethyl tartrate two terms of opposite sign are required.

Optical activity is later shown to be due to the presence of one or more optically active absorption bands. Thus in the case of transparent compounds the phenomenon of rotatory dispersion may be attributed to a band situated in the ultra violet region of the spectrum, but if such an asymmetric molecule possesses more than one optically active absorption band 'anomalous' rotatory dispersion results due to the superposition of PARTIAL ROTATIONS.

#### ROTATORY DISPERSION in the REGION of ABSORPTION.

When measurement of rotatory dispersion is made throughout an accessible optically active absorption band the resulting curve assumes a characteristically anomalous form and the phenomenon of CIRCULAR DICHROISM is observed. Such were the classical findings of Cotton<sup>3</sup> in 1896 when he investigated solutions of various coloured salts including copper tartrate in potassium hydroxide and the double tartrate of chromium and potassium.

In this case the optically active medium absorbs the two circularly polarised rays to different extents and on recombination these give rise to a resultant elliptically polarised beam (Circular Dichroism). Thus, for frequencies within an absorption band differences in both amplitude and

velocity of the two circularly polarised rays are produced with the result that rotation as well as ellipticity is developed. The latter quantity is given by  $\tan \phi = \frac{d - g}{d + g}$  where  $d$  and  $g$  are the amplitudes of the two circularly polarised components, i. e., is the ratio of the minor to the major axis of the elliptical vibration produced.

In detail, Cotton found on examination of his coloured solutions that the ellipticity varied with the wave length of light employed rising to a maximum at the head of the absorption band, while the rotatory dispersion possessed a maximum on the long wave side of the band and fell to zero at the head of the band. Such variation of rotation and ellipticity within an absorption band is known as the Cotton Effect.

Attempts were then made to determine the mathematical form of this really anomalous rotatory dispersion found within a region of selective absorption. The original Drude equation, previously used for transparent media failed signally in this case.

#### Correlation of ROTATION AND ABSORPTION.

We have seen that a relation appears to exist between the number of optically active absorption bands and the finally observed form of the curve of rotatory dispersion. Also mentioned is the fact that rotatory power depends upon the refractive indices,  $n_p$  and  $n_e$ , of the medium.

It was therefore to be expected that rotatory dispersion bears a similar relation to circular dichroism as refractive dispersion does to the absorption of unpolarised light. The latter relationship has long since been established as the Ketteler-Helmholtz<sup>4</sup> equation deduced from the Electromagnetic Theory of Light. A corresponding equation, connecting circular dichroism and rotatory dispersion was formulated in 1908 by Natanson<sup>5</sup>. Later, from an entirely different hypothesis, Kuhn<sup>6</sup> also deduced a relationship between these two phenomena.

Thus, if the circular dichroism of a medium has been investigated, the rotatory dispersion can be calculated from the position of the maximum and the half-width of the band on an analogous method to the calculation of refractive dispersion from the data of the corresponding absorption band. From this stage, henceforth, the path was clear to determine the extent to which an optically active absorption band, in an asymmetric molecule, contributes to the total optical rotatory power and thus to analyse the latter into its PARTIAL ROTATIONS.

For this purpose we will consider briefly some mathematical forms of curves of absorption and circular dichroism.

#### CURVES of ABSORPTION and CIRCULAR DICHRISM.

#### EXPERIMENTAL

Absorption curves are generally plotted as  $\epsilon = f(\lambda)$

where  $\epsilon$  is the observed molecular extinction coefficient defined by the relation  $\frac{I}{I_0} = 10^{-\epsilon c l}$ , where  $c$  is the concentration in gm.mols./litre and  $l$  is the thickness in cms. of a layer of solution.

Curves of circular dichroism are experimentally represented by the equation  $(\epsilon_e - \epsilon_r) = f(\lambda)$  where  $\epsilon_e - \epsilon_r$  is the difference of molecular extinction coefficients for the two circularly polarised rays. We have seen that the ellipticity is given by  $\tan \phi = \frac{d - g}{d + g}$  where  $d$  and  $g$  are the amplitudes of the two components.

By a simple step this becomes  $\tan \phi = \frac{1 - e^{-\frac{(\mu_e - \mu_r)t}{2}}}{1 + e^{-\frac{(\mu_e - \mu_r)t}{2}}}$  and when the angle  $\phi$  is small  $\phi$ , in radians, can be put for  $\tan \phi$ .

Thus we have  $\phi = \frac{(\mu_e - \mu_r)t}{4}$  and expressed in molecular extinction coefficients this becomes,

$$\phi = \frac{(\epsilon_e - \epsilon_r)t.c}{4 \cdot 0.4343}$$

This is the equation used to determine  $(\epsilon_e - \epsilon_r)$  in terms of the measurable quantity  $\phi$ .

In actual practice, the method of observing  $\phi$  is to superpose upon the unknown ellipticity a known ellipticity of opposite sign and may be measured in the visible by using a quarter wave plate suitably oriented, in conjunction with an ordinary polarimeter<sup>7</sup>.



THEORETICAL FORMS.

The Ketteler-Helmholtz<sup>4</sup> absorption equation, deduced on the assumption that light absorption is due to a frictional damping between atomic oscillators gives rise to the following,

$$\epsilon = \frac{\text{Const. } \lambda^2}{(\lambda^2 - \lambda_0^2)^2 + \Gamma^2 \lambda^2}$$

where  $\lambda_0$  is the wave length of maximum absorption and  $\Gamma$  is a damping factor. This equation holds only for narrow bands and was successfully used by Bruhat<sup>8</sup> and Pauthenier in the analysis of the absorption band of carbon disulphide by splitting it up into several narrow components.

Bielecki and Henri<sup>9</sup> next drew attention to the fact that an absorption curve can be represented by the empirical exponential equation

$$\epsilon = \alpha \nu e^{-\beta(\nu_0 - \nu)^2}$$

where  $\alpha = \epsilon_{\text{max}} \nu_0$  and  $\beta$  is a constant embodying the half width of the band.

Curves calculated from this equation for the absorption of compounds such as acetone, acetic acid and acetaldehyde bear quite close agreement with the experimentally observed curves. In this case the theoretical forms are unsymmetrical with respect to both frequencies and wave lengths.

Dissatisfied with the application of either of the

foregoing equations to their experimental data, Kuhn and Braum<sup>10</sup> formulated the equation

$$\epsilon = \epsilon_{\max} e^{-\left(\frac{\nu_0 - \nu}{\theta}\right)^2}$$

where  $\theta$  is a parameter embodying

the half width of the band. Absorption curves calculated from this equation are found to be symmetrical only on a scale of frequencies. Later, however, Lowry and Hudson<sup>11</sup> pointed out that, in general, absorption curves of chemical molecules are never quite symmetrical when expressed on a scale of frequencies but are invariably either symmetrical on a wave-length scale or are steeper on the side of longer wave lengths. To conform with these experimental observations they developed the relation

$$\epsilon = \epsilon_{\max} e^{-\left[\frac{\nu_0}{\nu} \left(\frac{\nu_0 - \nu}{\theta}\right)\right]^2}$$

This equation was successfully applied to compounds containing the chromophoric groups  $>C = O$  and  $>C = S$ . Comparison of the results obtained by using all the above equations in the fitting of the first absorption band of methyl d-bornyl-xanthate and others may be seen in a paper by Lowry and Hudson<sup>11</sup>.

#### Curves of Circular dichroism.

The ratio of circular dichroism to absorption,  $(\epsilon_2 - \epsilon_1)/\epsilon$  is defined as the anisotropy factor of the medium and is usually denoted by  $g$ . Deductions from the analogous equations of Ketteler-Helmholtz for absorption and of

Natanson for circular dichroism, which is mentioned below, lead to the result that this factor is, within an absorption band, proportional to the frequency of the light. Thus

$$g = \frac{2e\nu}{\nu_0}$$

Prompted by Cotton's discovery of circular dichroism, Natanson deduced an equation of the form

$$(\epsilon_c - \epsilon_r) = \frac{2Df\lambda}{(\lambda^2 - \lambda_0^2)^2 + f^2\lambda^2}$$

to represent the experimentally observed curves. This will be dealt with later when we come to consider the calculation of rotations.

Since  $(\epsilon_c - \epsilon_r) \epsilon$  is proportional to the frequency, curves of circular dichroism can therefore be represented by analogous equations to those obtained above for absorption.

Thus on the basis of the Lowry and Hudson equation there follows the relation,

$$(\epsilon_c - \epsilon_r) = (\epsilon_c - \epsilon_r)_{\max} \frac{\nu}{\nu_0} e^{-\left[\frac{\nu_0}{\nu} \left(\frac{\nu_0 - \nu}{\theta}\right)\right]^2}$$

and from the Kuhn and Braun equation we obtain the following

$$(\epsilon_c - \epsilon_r) = (\epsilon_c - \epsilon_r)_{\max} \frac{\nu}{\nu_0} e^{-\left(\frac{\nu_0 - \nu}{\theta}\right)^2}$$

In representing the curve in the case of potassium chromium tartrate, Kuhn and Szabo<sup>12</sup> found that they obtained a better result by omitting the factor  $\frac{\nu}{\nu_0}$  from the latter equation and thus used a relation similar to the absorption

equation of Kuhn and Braun. Further examples of the application of these equations may be found in Lowry's "Optical Rotatory Power".

CALCULATION of PARIAL ROTATION in the REGION of ABSORPTION.

The mathematical form of a rotatory dispersion curve in a transparent region given by Drude was later, in 1906, extended by the same author into the region of absorption. The equation thus obtained accounted for the phenomenon of circular dichroism but was not expressed in a form suitable for application to experimental data.

In 1908, Natanson<sup>5</sup>, from a mathematical consideration of the forced vibrations of an electron in an optically active molecule, under the influence of the electric vector of an incident plane polarised light ray deduced expressions for the rotation and ellipticity produced.

The rotation equation is  $\theta = \frac{D(\lambda^2 - \lambda_0^2)}{(\lambda^2 - \lambda_0^2)^2 + \Gamma^2 \lambda^2}$  and we have already mentioned the corresponding equation for circular dichroism.

To test these equations, Natanson himself calculated theoretical curves from Cotton's measurements of the rotatory dispersion and circular dichroism of the double tartrate of potassium and chromium and copper tartrate in potassium hydroxide solution.

According to the derivation of these equations, as given in his original paper, the damping factor  $\Gamma$  is equal

to  $\frac{\lambda_0^2 - \lambda_m^2}{\lambda_0}$  where  $\lambda_0$  is the wave length for which the rotation  $\theta$  is zero and  $\lambda_m$  is the wave length at which the rotatory dispersion curve has a maximum. Assuming  $\lambda_0$  and  $\lambda_m$ , a value for  $\Gamma$  was obtained and using four observed rotations and this value for  $\Gamma$  the constant D was evaluated. He then calculated eleven values for the rotatory dispersion according to the above equation and obtained a resultant curve satisfactorily resembling the observed curve of Cotton. It may be noted that  $\Gamma$  is numerically equal to the half width of the band of circular dichroism and so rotatory dispersion can be calculated from this data.

Kuhn's Theoretical Relation between Circular Dichroism and Partial Rotatory Power.

Working on a special case of Born's theory of coupled electronic vibrators, which will be mentioned later, Kuhn, in 1929, derived a more practical equation. As his molecular model, he employed two anisotropic rectilinear oscillators and by a simple description of the ensuing motion he demonstrated the essential features of optical activity. The resulting equations of motion were then used to prove the fact that the model behaves differently if irradiated with left or right handed circularly polarised light, thus demonstrating the association of optical rotatory power and circular dichroism.

Quantitative discussion led to the result that the contribution to the optical rotation by an absorption band

( $\xi_1$ ) whose frequency is  $\nu_1 = \frac{c}{\lambda_1}$  and whose half width is  $\nu_1' = \left(\frac{c}{\lambda_1} \lambda_1'\right)$  is expressed in angle of rotation and wave length,

$$\phi_{\xi_1} = \frac{\lambda^2 - \lambda_1^2}{(\lambda_1^2 - \lambda^2)^2 + \lambda^2 \lambda_1^2} \alpha_1 \lambda_1^2$$

He next obtained a corresponding relation for circular dichroism and by combining the two arrived at another equation which when integrated over the absorption band led to the final result

$$[M] = \frac{100}{2\sqrt{\pi}} \cdot \frac{(\xi - \xi_1)_{\max}}{\log_{10} e} \cdot \frac{\nu}{\nu_0} \left[ e^{-\left(\frac{\nu_0 - \nu}{\theta}\right)^2} \int_0^{\frac{\nu_0 - \nu}{\theta}} e^{x^2} dx - \frac{\theta}{2(\nu_0 + \nu)} \right]$$

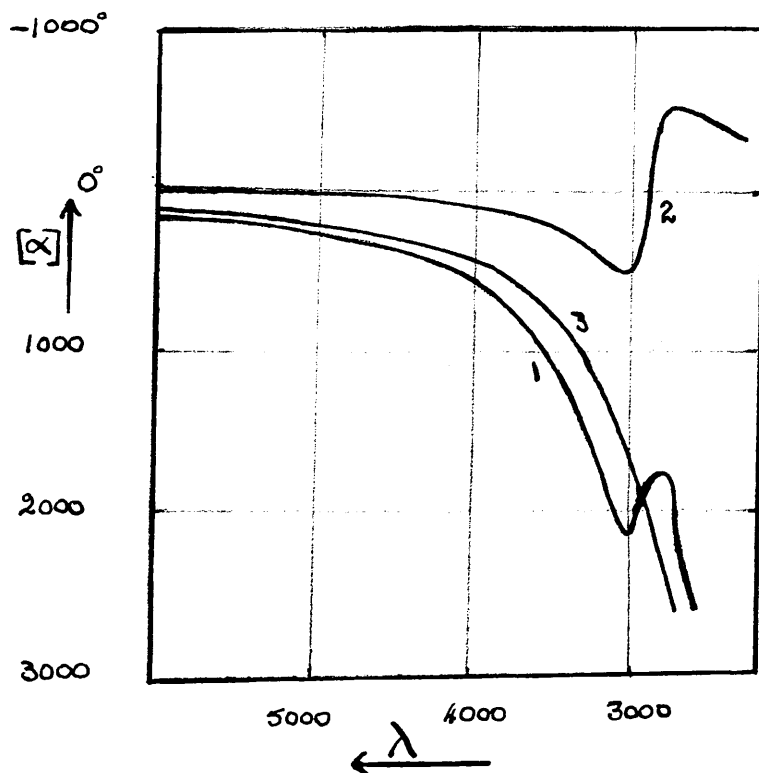
where  $[M]$  is the Molecular Partial Rotation and  $\xi$  is the maximum value of circular dichroism occurring at frequency  $\nu_0$ .  $\theta$  is the parameter embodying the half width of the dichroism band to which reference has already been made.

In the deduction of this equation it is important to notice that use is made of the form of circular dichroism curve previously formulated by Kuhn. Thus, in the calculation of partial rotations, values of  $\nu_0$  and  $\theta$  are taken from the corresponding curve of circular dichroism. In the absence of this data, however, calculation can be made from the curve of absorption by giving  $\theta$  an arbitrary value.

By means of the above relation Kuhn<sup>13</sup> and his collaborators calculated rotatory contributions in molecules containing the absorption groups  $N_3$ ,  $ONO$ ,  $Ph$ ,  $Cl$ ,  $Br$  and  $I$ . An example of the result obtained for the compound

$\alpha$ -azidopropionic dimethylamide,  $N_3 \cdot CH(CH_3) \cdot CO \cdot N(CH_3)_2$  is given in Fig. a. Curve 1 represents the observed rotatory dispersion which possesses an anomaly about  $\lambda$  2900, the wave length of maximum absorption due to the azido group. Curve 2 gives the form of the calculated rotatory dispersion found from the absorption data and curve 3 is the difference curve obtained by subtraction of the partial rotation from the observed. The residual curve thus obtained does not show any sign of anomaly due to the  $N_3$  chromophoric group and represents the remaining rotations due to more distant bands in the ultra violet region.

Fig. a.  $\alpha$ -azidopropionic dimethylamide.



Later, Lowry and Hudson<sup>11</sup>, to suit their own requirements, modified Kuhn's equation by incorporating their absorption equation and when converted to wave lengths the final equation has the form

$$[M] = \frac{100}{2\sqrt{\pi}} \cdot \frac{(\epsilon_e - \epsilon_r)_{\max}}{\log_e e} \cdot \frac{\lambda_0}{\lambda} \left[ e^{-\left(\frac{\lambda - \lambda_0}{\sigma}\right)^2} \int_{\frac{\lambda - \lambda_0}{\sigma}}^{\frac{\lambda + \lambda_0}{\sigma}} e^{x^2} dx + \frac{\theta}{2(\lambda + \lambda_0)} \right]$$

This equation is therefore based on the fact observed by these authors that absorption curves possess a more symmetrical form when plotted on a scale of wave lengths rather than frequencies. In investigations of a number of xanthates containing the CS.S band particularly good results were obtained using this equation.

Fig. b. *l*-menthyl dixanthogenide.

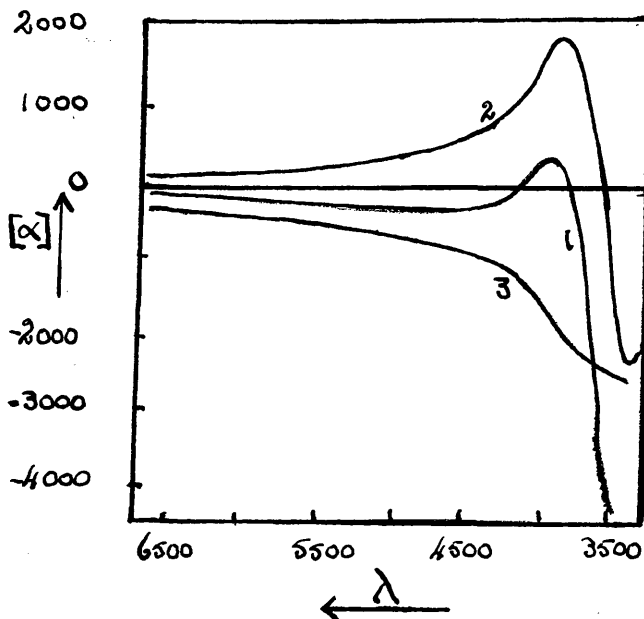
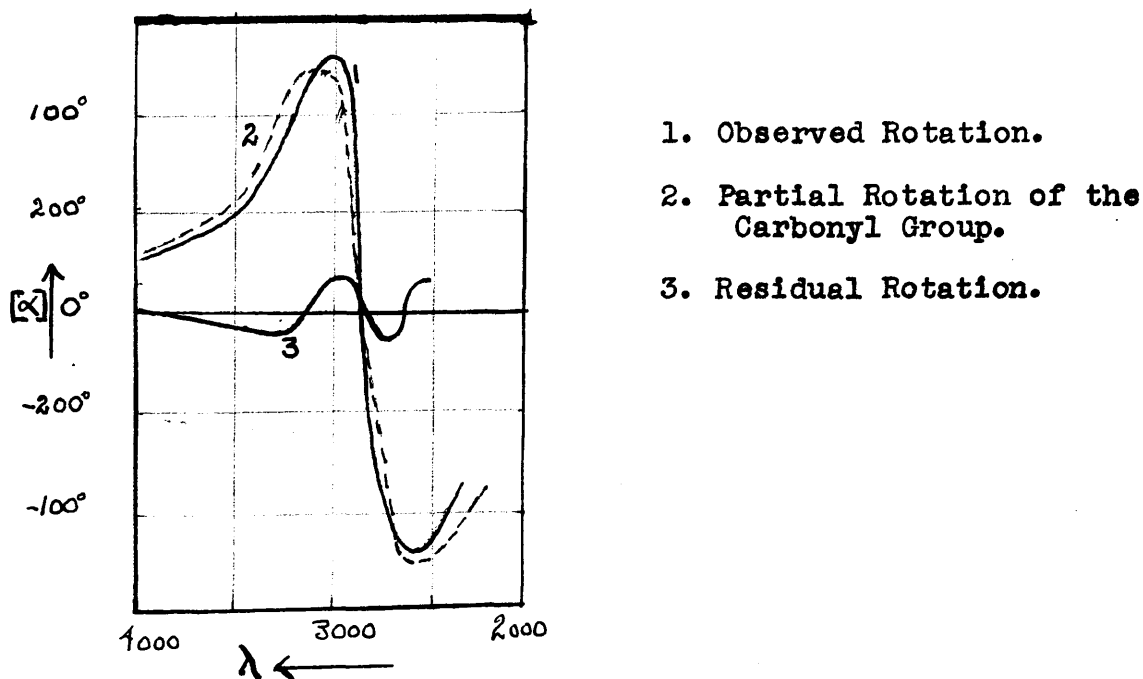




Fig.b gives an example of the Lowry and Hydson equation for *l*-menthyl dixanthogenide ( $C_{10}H_{19}O.CS.S$ )<sub>2</sub>. Curve 3 represents the residual rotation and of this Lowry says "the elimination of anomalies is more nearly complete than previous examples but it still leaves room for possible improvement."

Results, however, obtained later by Wolfram and Lowry<sup>14</sup> for compounds containing the CHO and CO group were not quite so satisfactory. For example, Fig.c shows the position in the case of penta-acetyl- $\mu$ -fructose.

Fig.c. penta-acetyl- $\mu$ -fructose.



Here the residual curve crosses the zero axis at several points. This is similar to a result obtained

recently by Mitchell and Gordon<sup>15</sup> when investigating the compound 2:2-dinitrocamphane in connection with the  $\text{NO}_2$  chromophoric group. They also made use of the above equation but failed to account for the entire anomalous rotation since the residual curve was not one of simple rotatory dispersion.

In Part II of this thesis an interesting and successful application of the above equation is described in the calculation of the partial rotation due to the NO group in the molecule. The absorption and circular dichroism curves of the compound described are of a composite character and an accurate analysis of these curves is made before proceeding to the estimation of the rotatory power due to the optically active band system. The residual curve obtained is free from all anomalies and bears comparison with the best of results obtained by previous investigators. This may be attributed to three facts:-

- (a) The absorption bands are situated near the middle of the visible spectrum with the result that a complete picture of the rotatory dispersion and circular dichroism can be obtained.
- (b) Measurements of the last two phenomena can be more accurately made in the visible than in the ultra violet where most of the previous compounds studied showed their absorption.

(c) The composite band structure was successfully analysed into two components which proved to be a major factor in the elimination of rotation anomalies.

#### Other Theories of Optical Activity.

Although the Kuhn equation functions satisfactorily in practice the validity of the hypothesis upon which it is based is open to question. Several theories of optical activity have been advanced both before and after the introduction of Kuhn's theory and we may do well to digress a little in order to complete the survey with a brief reference to the most important of these.

Born<sup>16</sup>, in 1915, enunciated a general theory of optical activity which has since been used as a basis for further deductions. This general theory pictures a molecule as a system of particles rigidly fixed relative to each other. By virtue of their properties these particles become electrically polarised when a ray of plane polarised light is incident upon the molecule. A field of force emanates from each of these particles and each in turn affects the other so that the resultant effect depends upon many separate interactions or couplings.

It was from this conception that Kuhn in 1929 developed his equation using as a molecular model two coupled anisotropic oscillators.

With the advent of quantum mechanics Born's theory was reformulated on the quantum mechanical interpretation of dispersion by Rosenfeld<sup>17</sup> and Born and Jordan<sup>18</sup>. The main conclusion drawn, however, was that the "rotation effect is due to the same set of virtual oscillators which determine the (refractive) dispersion. Therefore it is possible to replace the quantum mechanical system by a classical one, consisting of a set of harmonic resonators coupled by electric and magnetic forces."<sup>19</sup>

On the basis, therefore, of four non-planar coupled isotropic electrons, Born<sup>20</sup> has recently evolved a simplified formula from the general theory but due to the limitation of obtaining the required experimental data for constants it does not find much application.

Theories based more upon the chemical structure of the molecule rather than on a vibrating electronic system were advanced at different times by Gray<sup>21</sup>, De Malleman<sup>22</sup> and Boys<sup>23</sup>. Each attempted, with varying measures of success, to predict the optical rotatory power of a molecule in terms of the size, configuration and polarisabilities of its constituent groups. Thus an application of Boys' formula to sec-butylamine gives a calculated rotation  $[\alpha]_D = 7.4$  while the observed value is 7.44, and to sec-butyl alcohol  $[\alpha]_D$  calc. = 9.3 and  $[\alpha]_D$  obs. = 13.9.

In 1937, Kirkwood<sup>24</sup> has shown how the quantum

mechanical formulation of Born's theory leads to the polarisability theory of those authors last mentioned, and the formula he obtained was applied to sec-butyl alcohol with good results.

About the same time Condon, Altar and Eyring<sup>25</sup> showed that a single electron moving in a field of suitable dissymmetry can give rise to optical rotatory power. This effect is in striking contrast to Born's conception that only coupled vibrators can produce optical activity. The former theoretical basis is called "one electron rotatory power". Their theory was illustrated by the calculation of the contribution of the nitrite group to the rotatory power of methyl phenyl carbinol nitrite which agreed well with experimental data. They also calculated the phenyl group contribution in this molecule and the contribution of the OH group in sec-butyl alcohol, but the values obtained were rather small.

A completely infallible physical explanation of optical activity has not yet been forthcoming, but results up till now have been encouraging and point to the likelihood of future success. From the point of view of the chemist, however, the most satisfactory theoretical relation so far deduced is that formulated by Kuhn, the consequences of which have already been described.

Circularly Polarised Light as a means of producing Optical Activity.

Before the digression in the last section we have seen how the presence of a chromophoric group in an optically active molecule gives rise to anomalous rotatory dispersion and circular dichroism. This latter property arises from the unequal absorption of the two forms of circularly polarised light; the converse of this might also be expected to be true - that two optically active isomers will absorb one form of circularly polarised light to different extents.

The absorption of unpolarised light by chemical compounds is a subject which has received a great deal of study within recent years, but for the present purpose we shall consider only the selective absorption of light by organic molecules in solution. When such a substance absorbs a quantum of light there may be one of several consequences:

- (1) It may return to its original energy state with emission of light, i.e., it may exhibit fluorescence, as is the case with a number of organic dyestuffs.
- (2) The molecules of the compound after activation, either dissociate or react with other molecules.
- (3) The entire absorbed energy may be converted into translational kinetic energy by collision with other molecules.

If we consider a compound from group (2) which is chemically decomposed by the absorbed light quanta then it follows, that if it can exist in an optically active form which exhibits circular dichroism within a region of selective absorption, the irradiation of the racemic mixture with one form of circularly polarised light of suitable frequency should result in the more rapid destruction of one optical isomer. Optical activity in the original racemic mixture would then be produced.

The possibility of thus producing optical activity was theoretically opened by Cotton<sup>3</sup>, who in his original paper pointed out this fact as a possible application of his discovery of circular dichroism. Cotton<sup>26</sup>, himself, made an unsuccessful attempt to produce an optical rotation in a solution of copper racemate by this means. His failure was due, however, to the fact that this compound is not decomposed by the same absorption of red light which results in the observed circular dichroism. The compound can only be decomposed by ultra violet light of frequencies for which solutions of copper d-tartrate were later shown by Mitchell<sup>27</sup> to exhibit no difference of absorption for the two types of circularly polarised light.

The first measure of success was not achieved until 1929, when Kuhn and Braun<sup>28</sup>, after a study of the rotatory dispersion and circular dichroism in the ultra violet, of the active form of ethyl  $\alpha$ -bromopropionate, subjected a

solution of the inactive form to the decomposing effect of one form of polarised light with the resultant production of optical activity.

Soon after this, Kuhn and Knopf<sup>29</sup>, following a similar study of the compound  $\alpha$ -azidopropiondimethylamide, contrived, by irradiation of a solution of the inactive compound, to produce an observed rotation of the order of  $1^\circ$ .

The anisotropy factor, which we have previously found to be the ratio of circular dichroism to absorption of unpolarised light was found in the case of the latter compound to be .024. It may readily be appreciated that this factor, which is a measure of the relative absorptions of two optically active isomers, exerts a powerful influence in the determination of the suitability of a compound for use in an asymmetric photochemical decomposition.

While the above two experiments were in progress, Mitchell<sup>27</sup> had begun an investigation of caryophyllene nitrosite with a view to effecting such a decomposition. This compound was found to exhibit circular dichroism in the red end of the spectrum due to the presence of the nitroso group and possessed the rather abnormal anisotropy factor<sup>30</sup> of .12. Such a compound was therefore considered to be very suitable and by irradiation of a solution of the inactive nitrosite of the analogous compound humulene, rotations of +.30 and -.30 were developed for the two forms of circularly polarised light.

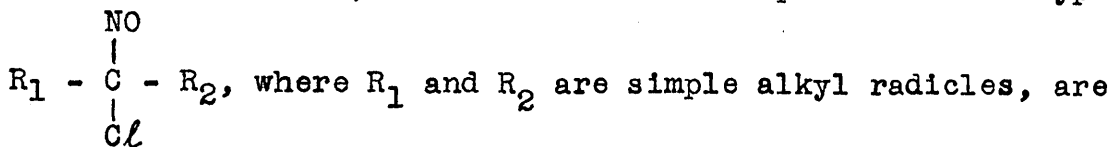


As a consequence of this last successful attempt, a search was made for a more simple type of asymmetric compound containing the nitroso group, which might be advantageously investigated and used in this connection. That is, a search was conducted for a simple type of nitroso compound which is decomposed by light and which may be obtained in an optically active form. This latter condition is necessary so that a study of the rotatory dispersion, circular dichroism and anisotropy factor can be made.

Along these lines, a study of pseudo-nitrols and some simple nitroso compounds, both secondary and tertiary, was carried out in these laboratories by Dr. Mitchell and his collaborators<sup>31</sup>. Many interesting facts emerged from these investigations and an optically active nitroso compound was eventually prepared by Mitchell and Carson. This is the compound  $\alpha$ -methyl  $\alpha$ -nitroso- $\eta$ -butyrate which was obtained by oxidation of active  $\alpha$ -methyl  $\alpha$ -amino- $\eta$ -butyrate previously made from active isovalin. The specific rotation of this substance for the D line was, however, only of the order of  $10^0$ . Solutions of the compound showed no circular dichroism, although a slight anomaly in the rotatory dispersion was detected in the region of absorption.

The next type of simple nitroso compound to be studied was the chloro-nitroso compound. Of the few compounds of this group that have been prepared, almost all are blue in colour and possess an absorption band in the red region of the spectrum.

Such compounds appeared to be suitable for use in asymmetric photochemical work and in the first part of the preliminary investigations towards this end Mitchell and Cameron<sup>32</sup> undertook a study of the photochemistry of some of these compounds. In the experiments, carried out in these laboratories, it was found that compounds of the type



decomposed by light with the destruction of the asymmetric centre. These authors also developed a technique for measuring the quantum yield of the photolysis by red light.

This now brings us to the present problem described in this thesis - namely, the attempt to prepare an optically active chloronitroso compound so that a study can be made of the rotatory dispersion and circular dichroism within the region of photochemical absorption. From this, a value of the anisotropy factor for such a compound can be obtained and so enable us to assess the likelihood of effecting an asymmetric photochemical decomposition.

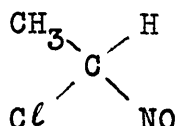
Attempts to prepare an optically active chloronitroso compound necessitated the making of new compounds of this group, among which are the first two aliphatic nitroso acids known to exist in the blue monomeric form. Direct resolution of these acids by means of an optically active base was tried without success, but when investigating menthyl

esters of such acids the first signs of optical activity due to the asymmetric chloro-nitroso centre became apparent. This is described fully in the first two parts of the thesis. In the latter part is a description of some photochemical aspects of the new compounds concerned and includes an effective modification of the method, recently developed in the department, for measuring quantum yields of photolyses with red light.

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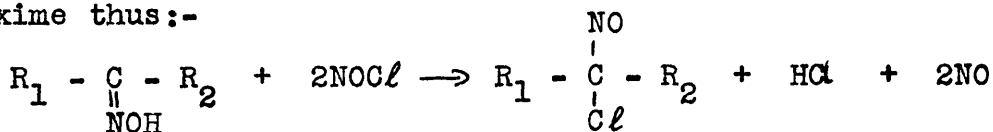
PART I.Preparation of an Optically Active Chloronitroso Compound.

The first recorded preparation of a chloro-nitroso compound was that done by Piloty and Steinbock<sup>33</sup>. The substance is monochloro-nitroso ethane,

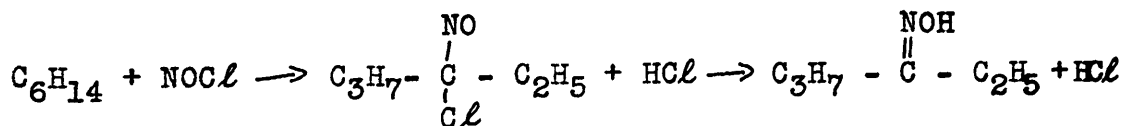


and was obtained by the action of chlorine on acetaldoxime. In this case, as in other secondary nitroso compounds, the colourless, bimolecular form is obtained.

Compounds of the type  $R_1 - \begin{array}{c} \text{NO} \\ | \\ \text{C} \\ | \\ \text{Cl} \end{array} - R_2$ , where  $R_1$  and  $R_2$  are simple alkyl radicles were made by Rheinboldt and Dewald<sup>25</sup> by the action of nitrosyl chloride on the corresponding oxime thus:-



Mitchell and Carson<sup>34</sup> obtained chloronitrosohexanes by the action of nitrosyl chloride on hexane under the influence of light. This reaction is similar to that of Rheinboldt above, since the first stages of the reaction are



The compounds obtained were,

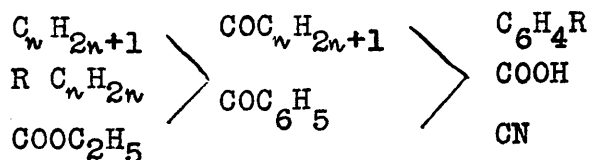
$\text{CH}_3\text{C}(\text{Cl})(\text{NO})\text{C}_4\text{H}_9$   $\beta\beta$  chloronitroso hexane  
and  $\text{C}_3\text{H}_7\text{C}(\text{Cl})(\text{NO})\text{C}_2\text{H}_5$   $\gamma\gamma$  chloronitroso hexane

These are the only two chloronitroso derivatives of  $n$ -hexane in which the nitroso group is not attached to the same carbon as a hydrogen atom.

The compounds can also be obtained by the action of chlorine on the oxime and this was the method used by Mitchell and Cameron<sup>32</sup> in the preparation of some chloronitroso derivatives of the paraffins.

De Paolini<sup>35</sup> records a number of attempts to prepare bromo-nitroso derivatives of certain compounds by the action of bromine on the oxime. He did not investigate the compounds further than observing the appearance of a blue colouration.

The general result obtained was that compounds containing the groups COOH, CN,  $C_6H_5$  or substituted phenyl adjacent to the oxime group did not form bromo-nitroso derivatives by the action of bromine. A classification of different groups adjacent to the oxime group which favour formation of the blue compounds may be given thus



It is found that this rule also applies to the formation of chloro-nitroso compounds.

Preparation of some chloro-nitroso compounds.

Since the obvious method to obtain an optically active compound is by the resolution of an acid by a suitable base, attention was directed to the possibility of preparing a chloro-nitroso acid. No aliphatic nitroso acids had hitherto been isolated in a stable form. Such acids are invariably unstable and easily change over to the corresponding oxime. In the course of this work, however, the first two aliphatic nitroso acids to exist in the monomeric form have been prepared. These compounds are blue solids.

 $\gamma$ -chloro  $\gamma$ -nitroso valeric acid.Preparation.

The preparation of this compound was attempted due to the fact that it may be derived from laevulinic acid, a substance easily obtainable from cane sugar. A large quantity of laevulinic acid was prepared and converted into the oxime. This was dissolved in dilute hydrochloric acid solution and ether added. The flask was placed in a freezing mixture and a stream of chlorine gas passed into it, resulting in a blue colouration of the ether layer. The latter was washed with potassium bicarbonate solution until the aqueous layer took on a slightly blue tinge. After drying the blue ethereal solution over anhydrous sodium sulphate the ether was removed under reduced pressure. A blue non-distillable oil remained, but when left in thin layers in a cold atmosphere it crystallised out in blue

plates. It can be recrystallised from hexane. Blue plates, m.p. 33°.

Analysis of the acid after purification by recovering it from the ephedrine salt gives the following:-

Experimentally: Cl(21.24%); C(36.22%); H(4.92%); N(8.67%)  
 $C_5H_8O_3NCl$  requires: Cl(21.42%); C(36.36%); H(4.90%); N(8.46%).

The compound prepared by the action of chlorine on the oxime of laevulinic acid, with liberation of HCl is therefore γ chloro γ nitroso valeric acid,  
 $CH_3C(Cl)(NO).CH_2.CH_2.COOH$ .

This acid is sparingly soluble in water, but is soluble in most organic solvents.

The yield obtained by the above method is only 5% of chloro-nitroso compound calculated on the oxime. After several experiments, the yield was increased to about 30% by simply dissolving the oxime in dry ether and passing in chlorine; the remainder of the method is as described above.

Methyl chloro nitroso valerate. This compound can be prepared by the action of chlorine on the oxime of methyl laevulinate. It is a blue liquid, b.p. 84°C/20 mms.

<u>Analysis</u>	<u>Chlorine estimation</u>
Exp. (Stepanow)	19.59%
Theor.	19.75%

α chloro α nitroso propionic acid. The attempted preparation of this compound from pyruvic acid oxime resulted

in the formation of a green oil.

Thus compounds of the type  $R.C.COOH$  do not form stable chloro nitroso compounds. This may be due to the additive property of the compound  $R.C \begin{array}{c} \parallel \\ NOH \end{array} C - OH$ . If, however, the acid group is esterified (e.g., the oxime of the menthyl ester of pyruvic acid) then the chloro-nitroso compound is quite definitely blue and stable.

Various attempts to prepare the chloro-nitroso acid corresponding to aceto acetic acid met with no success.

Outlines of the methods attempted are:-

(a) The oxime of acetoacetic ester was prepared and treated with ammonia, yielding solid methylisoxazolone. It has been presumed that the oxime of acetoacetic acid  $CH_3C = NOH.CH_2COOH$  is present in an aqueous solution of this compound but it was found that no blue colouration resulted on passage of chlorine. Hence either the oxime of the acid is not present in solution or else the chloro nitroso compound is non-existent.

(b) 28 gms. acetoacetic ester were hydrolysed for 24 hours with  $2\frac{1}{2}\%$  KOH solution in 500 ccs. water. Acidified strongly with  $H_2SO_4$  and extracted with ether; the ether removed cautiously, and  $BaCO_3$  and water added gives rise to strong effervescence. Any unchanged ester was extracted with ether leaving an aqueous solution of the Ba salt of acetoacetic acid. The oxime of this salt was then formed and



HCl added to set free the oxime of the acid. This was extracted with ether. Passage of chlorine resulted in a green oil which on standing produced yellow crystals, probably of methylisoxazolone.

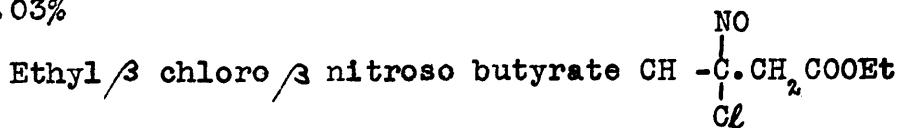
(c) Ethyl  $\beta$  chloro  $\beta$  nitroso butyrate and attempted hydrolysis to  $\beta$ -chloro  $\beta$  nitroso butyric acid.

The oxime of acetoacetic ester prepared by means of aniline and hydroxylamine hydrochloride is almost exactly the theoretical amount of a red oil. This oil goes solid by internal condensation and must be freshly prepared for use.

The action of chlorine on an acidified (HCl) aqueous solution of the oxime results in the production of a blue liquid. When extracted with ether, etc., and finally distilled, it was found to be a deep blue pungent liquid of b.p. 80°/18 mms.

Chlorine estimation by Stepanow's method gave

Cl = 20.03%



requires Cl = 19.75%.

This compound has a narrow absorption band in the red and is decomposed to give mainly the oxime and hydrochloric acid when exposed to red light in the absence of oxygen.

For hydrolyses purposes it is unfortunate that this compound, in common with the others in the chloro nitroso group, is decomposed by alkali or by prolonged heat. Consequently only acid hydrolysis at moderate temperatures could be attempted. Various trials, using hydrochloric and sulphuric acids, however, did not give the desired result.

It may be mentioned here that methyl /3 chloro /3 nitroso butyrate is rather difficult to obtain pure due to the fact that, like the parent acid, the oxime rapidly goes solid by internal condensation producing with chlorine only a green oil which when distilled yields a diluted blue compound boiling at 80°/30 mms. and 100°/72 mms. (with decomposition). The blue compound is contaminated with some colourless compound as accurate analyses cannot be obtained.

αα dimethyl /3 chloro /3 nitroso butyric acid.

Since the possibility of resolving an acid by a base may be adversely influenced by the length of the chain from the asymmetric centre, it was decided that rather than investigate the acid beyond laevulinic acid in the series an attempt to prepare a derivative of a substituted acetoacetic acid would be more advantageous.

Accordingly, αα dimethyl aceto acetic ester<sup>36</sup> was prepared and the oxime formed. The oxime was then decomposed by concentrated sodium alcoholate with the production of an insoluble sodium salt. The salt was decomposed by

dilute sulphuric acid and the free crystalline acid oxime extracted with ether, m.p.  $96^{\circ}$ . From 60 gms. of acetoacetic ester about 5 gms. of the acid oxime were obtained.

### Action of Chlorine.

When the oxime was dissolved in dilute hydrochloric acid and ether added, a blue compound appeared to form with the passage of chlorine. The ethereal layer was washed with water and potassium bicarbonate solution and after drying, the solvent was removed. A blue solid remained. Recrystallised from methyl alcohol it had m.p.  $150^{\circ}$  (Decomp.).

### Analysis:

Experimentally: Cl (19.58%); C (39.49%); H (5.61%)  
 $C_6H_{10}O_3NCl$  requires: Cl (19.77%); C (40.11%); H (5.56%).

Thus, the compound produced is  $\alpha\alpha$  dimethyl  $\beta$  chloro  $\beta$  nitrosobutyric acid,

$$\begin{array}{c} \text{NO} \\ | \\ \text{CH}_3 - \text{C} - \text{C}(\text{CH}_3)_2 \cdot \text{COOH} \\ | \\ \text{Cl} \end{array}$$

Unfortunately, the yield of this compound, calculated on acetoacetic ester as starting material, is very small.

Properties. The acid is sparingly soluble in water but is soluble in most organic solvents.

It gives a crystalline solid salt with  $\alpha$ -phenylethylamine in dry ether.

With ephedrine in dry ether the acid also gives rise to a blue solid salt, but owing to the difficulty of obtaining a sufficient quantity of the acid, these salts were not investigated further.

Salt Formation of  $\gamma$  chloro  $\gamma$  nitroso valeric acid.

The asymmetric carbon atom in this acid is in the gamma position and is rather distant from the carboxyl group. It has been noted, however, that such an asymmetric centre can be resolved, c.f.,  $\gamma$  amino valeric acid which was resolved by Fischer<sup>37</sup> using quinine.

A large amount of the chloronitroso acid was prepared using cane sugar as starting product. Many attempts to form salts with optically active bases were made but the majority proved fruitless. Due to the presence of the chlorine atom in the molecule, no doubt, many of the bases caused decomposition. On the other hand, several cases were successful and in each, it may be noted, the base employed was of low molecular weight. A brief account of the attempts are given below.

Brucine, m.p. 178°. Formation in various solvents resulted in the production of a blue oil which rapidly decomposed.

Quinine, similar to above.

Codeine (morphine methyl ether), m.p. 155°. No salt formation.

Strychnine, m.p. 284°. Produced an oil from methyl alcohol and chloroform.

Cinchonine, m.p. 255°. No salt formation.

Pseudoephedrine, m.p. 118°. Resulted in a blue oil.

Colicantyne forms a salt in dry ether which rapidly turns green.

Quinidine, produces an oil.

Successful Attempts.

(A) Ephedrine alkaloid  $C_6H_5 \cdot CH(OH) \cdot CH \cdot (CH_3) \cdot NH \cdot CH_3$ ,

mol. wt. 165. m.p.  $40^\circ$ .

The acid was dissolved in dry ether and ephedrine added in molecular proportions: on shaking, a pale blue salt separated out. The salt, washed with ether and dried, had m.p.  $80^\circ C$ . (Dec.).

The salt is very soluble in water, acetone, dioxane, carbon tetrachloride and propyl alcohol.

Attempted recrystallisation from chloroform, methyl alcohol, ethyl alcohol and other solvents produced an oil.

Ether proved to be the only solvent from which crystals would appear but due to the low solubility of the salt in ether this is not a very practicable medium.

Using ephedrine of m.p.  $40^\circ C$ . and  $[\alpha]_{5461}^{18} = +16.01$  in water and  $[\alpha]_{5461}^{18} = -6.20$  in ethyl alcohol, the blue salt formed gave the following: Conc. .2107gms./10 ccs. water

$\lambda$	$\alpha$	$[\alpha]$
4658	.44	-20.88
5290	.44	-20.88

and for .2334 gms. in 10 ccs. ethyl alcohol

$\lambda$	$\alpha$	$[\alpha]$
4850	.84	-36
5290	.63	-27.

These readings show an interesting variation with

solvent. On recrystallising from ether, however, no change in the rotation could be detected. It is unfortunate that a solvent more suitable for recrystallisation cannot be found.

Analysis of the ephedrine salt.

Experimentally: C = 56.49% and H = 6.26%,

Theoretically: C = 54.48% and H = 6.96%.

The sample probably contained traces of ephedrine as impurity which cannot be properly eliminated.

$\gamma$  chloro  $\gamma$  nitroso valeric acid can be easily recovered from the ephedrine salt by decomposing with dilute HCl solution and extracting with ether. Recovered acid has m.p. 32°C.

(B)  $\beta$ -naphthol phenylaminomethane<sup>38</sup>.

This base, recovered from the tartrate salt, had m.p. 123°C.

Equivalent quantities of the base (in dry ether) and the blue acid (in dry ether) were mixed and almost immediately a pale blue salt was precipitated. M.p. 95°C (Dec.).

The salt is rather unstable. It is soluble in water and ethyl alcohol but is insoluble in ether, hexane and benzene. It may be recrystallised from alcohol or ethyl acetate, but decomposition rapidly occurs.

(C)  $\alpha$ -phenylethylamine immediately gives in ether a salt with the acid. It is soluble in water but insoluble in benzene. Blue needle-shaped crystals of m.p.  $88^{\circ}\text{C}$ . are obtained from ethyl acetate.

For use in a resolution, the  $\alpha$ -phenylethylamine must, of course, be optically active. A quantity of racemic base was prepared from acetophenone and resolved by means of tartaric and quinic acids, as indicated by Hopper<sup>39</sup>, who used malic acid instead of quinic acid. The quinic acid is employed for a partial resolution and the  $\ell$ -base is further resolved by means of d-tartaric acid. After six crystallisations the rotation of a 10% aqueous solution of the d-tartrate  $\ell$ -phenylethylamine salt had the value  $+1.1$  similar to that found by Hopper.

The active base recovered from the tartrate salt had  $[\alpha]_{\text{D}}^{18} = +8^{\circ}$  in alcohol, but no resolution in combination with chloro-nitroso valeric acid could be detected, probably due to the small rotational magnitude of the base.  $[\alpha]_{\text{D}}^{18}$  of salt in alcohol =  $-7.3^{\circ}$ .

#### Analysis of salt.

Experimentally: C = 54.76: H = 6.74: N = 9.05

Theoretically: C = 54.45: H = 6.63: N = 9.77.

(D) l-menthylamine.

L-menthone oxime was prepared from l-menthone<sup>40</sup>. By reduction of the oxime in alcohol l-menthylamine<sup>41</sup> was obtained, b.p. 209°.  $[\alpha]_D^{18} = -34.8^\circ$  in alcohol.

The laevo base thus obtained yields a blue salt in a dry ethereal solution of the chloro-nitroso acid.

The salt is soluble in alcohol,  $CCl_4$  and ethyl acetate. It recrystallises in large prisms from hexane. M.p. 102.5°C (Dec.).

A quantity of the salt was prepared and rotations taken after recrystallising.

	$\lambda$	$\alpha$	1 Dcm. tube.	Solvent alcohol
			Concntr.	$[\alpha]$
1st Crystallisation	5400	.40	.1331/10 ccs.	-30°
2nd "	5400	.20	.0590/10 ccs.	-33.9°
3rd "	5400	.40	.0996/10 ccs.	-40.16°

Although not far removed from the magnitude of experimental, the differences between these readings were encouraging. Another sample of the salt, however, when recrystallised several times showed no change from the original rotation

$\lambda$	$\alpha$	$[\alpha]$	1 Dcm. tube	} Concntr.
5400	.72	-40°	.6 Dcm. tube	

The recrystallised product gave for a concentration .1750 gms./10 ccs. alc. and in 6 cms. tube -



$\lambda$	$\alpha$	$[\alpha]$
5400	.40	-38.1°.

The chloro-nitroso acid can be recovered from the recrystallised  $\ell$ -menthylamine salt by decomposition with HCl solution. Crystals of the acid obtained had m.p. 32°C but showed no rotatory power.

Observations in this case as in those preceding are not easily carried out due to the intense absorption of the light and the small concentration this imposes with consequent diminution of the rotation angle, even when using as source a Hg arc lamp with green filter. From the foregoing results it is evident that a base with a high rotation would be advantageous in measuring such rotational magnitudes.

Having exhausted most of the likely bases, attention was diverted to the possibility of resolving the acid by means of the menthyl ester.

Menthyl  $\gamma$  chloro  $\gamma$  nitroso valerate.

Menthyl laevulinate<sup>42</sup> was prepared and from it the oxime formed. The solid oxime does not dissolve in dilute HCl solution, but is soluble in concentrated HCl and in ether. Chlorine gas passed through an ethereal solution of the oxime produced a strong blue colouration. On removing the ether a heavy blue oil remained. Attempts to freeze it or to crystallise it from various solvents failed. Other methods of preparation produced the same result, thus it may be concluded that this compound is not a solid and

is therefore of no use for the immediate problem of resolution.

Preparation of Bornyl and Menthyl esters of chloro-nitroso acids.

Continuing on the above line, attempts were made to obtain solid esters. All but  $\ell$ -menthyl  $\beta$  chloro  $\beta$  nitroso butyrate were found to exist as blue oils.

Compounds obtained as blue viscous oils.

$\ell$ -menthyl  $\alpha$ -chloro  $\alpha$ -nitroso propionate,  
 $\ell$ -menthyl  $\alpha\alpha$  dimethyl  $\beta$ -chloro  $\beta$ -nitroso butyrate,  
 $\ell$ -menthyl  $\delta$ -chloro  $\delta$ -nitroso valerate,  
d-bornyl  $\beta$ -chloro  $\beta$ -nitroso butyrate,  
d-bornyl  $\delta$ -chloro  $\delta$ -nitroso valerate.

For the above compounds the ketonic esters were prepared<sup>43</sup> and converted into the corresponding oximes. These oximes are soluble in concentrated HCl but are insoluble in dilute HCl solution. Various solvents for the oximes were used in attempts to obtain solid chloro-nitroso compounds but the members of the above list could only be got as heavy blue oils.

In the case of the menthyl esters it is interesting to note the following:-

		<u>Oxime</u>	<u>Chloro-nitroso Cpd.</u>
$\ell$ -menthyl pyruvate	Liquid	Solid	Liquid
$\ell$ -menthyl acetoacetate	Solid	Liquid	Solid
$\ell$ -menthyl laevulinate	Liquid	Solid	Liquid.

Thus in this series the ester of the acid next to laevulinic acid in the ketonic series may yield a solid chloro-nitroso ester. The length of the chain becomes rather long in this case.

In an attempt to load up the molecule the menthyl ester of dibenzyl aceto-acetic acid was prepared, but the corresponding chloronitroso compound could not be made, due to the fact that the intermediate oxime was unobtainable.

Preparation of (-) Menthyl 3 chloro 3 nitroso butyrate with subsequent resolution of the asymmetric carbon atom to which is attached the Cl and NO groups, with formation of (-) menthyl (+) 3 chloro 3 nitroso butyrate.

Menthyl acetoacetate<sup>44</sup> was treated with hydroxylamine hydrochloride and sodium acetate in aqueous alcohol. On standing overnight or on boiling off the alcohol, the oxime is obtained as a yellow oil.

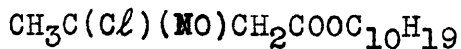
#### Action of chlorine.

To obtain the best results, it was found that the oxime should be dissolved in concentrated hydrochloric acid and water added. This results in an oily suspension. If kept at 0°C. and chlorine passed through, with occasional shaking, a blue oily solid forms. This blue solid is washed with water and dissolved in hot alcohol. On cooling, blue needle shaped crystals are formed. The blue ester is soluble in alcohol, ether, hexane, etc., but is insoluble

in water. It can readily be recrystallised from ethyl alcohol.

Analysis.

Experimentally: C(58.08%); H(8.23%); N(4.97%); Cl(11.9%)



requires: C(58.02%); H(8.28%); N(4.84%); Cl(12.2%).

Thus, the compound prepared is the menthyl ester of  $\beta$ -chloro  $\beta$ -nitroso butyric acid.

Resolution of the Menthyl Ester.

About thirty grams of the ester were subjected to repeated crystallisations from ethyl alcohol.

Record of Melting Points and Specific Rotations.

	<u>Conc.</u>	<u>Tube</u>	$\lambda$	$\alpha$	$[\alpha]$	<u>M. P.</u>
Crude Product	.0870g./10ccs.	(2cms.)	5200	--.27	-155.2	58-60°
2nd Crystallisn.	.0600g./10ccs.	(10cm.)	5250	-1.13	-188.3	-
3rd Crystallisn.	.0700g./10ccs.	(10cm.)	5250	-1.64	-234.2	-
4th Crystallisn.	.0528g./10ccs.	(10 cm.)	5250	-1.27	-240.5	67°
5th Crystallisn.	.0477g./10ccs.	(10cm.)	5250	-1.26	-264	-
6th Crystallisn.	.0442g./10ccs.	(10cm.)	5250	-1.47	-333	70°
7th Crystallisn.	.0491g./10ccs.	(6cm.)	5250	-0.94	-320	71°

With the eighth crystallisation the rotatory dispersion readings were found to be constant. Thus at this stage the resolution is complete. The fact that both the melting point and the rotations increase rather considerably points to the view that the crude product is the *d*l chloro-nitroso butyrate, while the final product is the *d* form of

the chloronitroso acid in combination with *l*-menthol. Additional proof that a resolution, and not merely a purification has been effected, is shown from the development of circular dichroism associated with the asymmetric C atom to which is attached the nitroso group.

Readings of both ellipticity and rotation in alcoholic solution for sodium light give,

$$(C = .6550\text{gms./}100\text{ccs.} : \ell = 6 \text{ cms. } t = 18^\circ)$$

	$\alpha_{5893}$	<u>Ellipticity</u>
Crude Product, m.p. 58-60°	-0.43°	+ (just detectable)
Final Product, m.p. 71°	-1.39	+1.41°

A similar instance to this compound has been recorded by Kägi<sup>45</sup>. He found that the m.p. of *l*-menthyl benzylacetoacetate increased with fractional crystallisation and after examining the rotations of his initial and final products he concluded that the former was the *dl*-benzylacetoacetate and the latter the *l*-ester.

The resolution of the chloro-nitroso asymmetric centre by the agency of *l*-menthol is partly comparable to those partial asymmetric syntheses performed by McKenzie and co-workers<sup>46</sup>. In one of these, atrolactic acid was obtained by a Grignard synthesis on (-)menthyl benzoylformate. In this case the laevo bias of the attached menthol and the choice of proper conditions resulted in the production of (-)menthyl(-)atrolactinate in excess. Saponification with potash, followed by removal of (-)menthol led to the formation of laevo rotatory atrolactic acid.

In the case of (-)menthyl(+)chloro-nitroso butyrate, however, the ester cannot be hydrolysed to the free acid and menthol. Chloro-nitroso compounds decompose in the presence of alkali and acid hydrolysis proved ineffective.

In the light of results which are fully discussed in the next part and from the point of view of asymmetric decomposition by circularly polarised light, some inactive compounds related to the menthyl ester were prepared.

Ethyl /3 chloro /3 nitroso butyrate

Described on pages

Methyl /3 chloro /3 nitroso butyrate

29,30

Cyclohexanol ester of chloro nitroso butyric acid was prepared in an attempt to obtain a solid product but resulted in a blue oil.

Cyclohexanol and acetoacetic ester were heated at about 160°C for 8 hours. From the fraction distilling at 155°C/40mms., 10 gms. were obtained. The oxime of this ester is a yellow oil and when acted upon by chlorine produces a heavy blue oil. This, as in other cases of blue oils, cannot be distilled since they decompose at temperatures above about 100°C.

Thymol ester. No blue colour developed; in this attempt, however, it was doubtful if the thymol ester of acetoacetic acid was prepared at all by this method.

Summary.

In the foregoing, the preparation and properties of some chloro-nitroso compounds have been described. Such compounds possess an absorption band in the red end of the visible spectrum and can be decomposed by light of the absorption frequencies.

The two chloro-nitroso acids prepared,  $\gamma$  chloro  $\gamma$  nitroso valeric acid and  $\alpha\alpha$  dimethyl  $\beta$  chloro  $\beta$  nitroso butyric acid, are the first aliphatic nitroso acids found to exist in a stable state. With a view to effecting a resolution, a study of salts with various bases and alkaloids was carried out and several such compounds were prepared. Repeated crystallisations of these salts, however, failed to produce any detectable optical activity in the acid.

Another important compound described is the blue crystalline menthyl ester of chloro nitroso butyric acid. When recrystallised seven or eight times from ethyl alcohol the melting point rises from  $58^{\circ}$  to  $71^{\circ}$ , and the specific rotation increases by about  $300^{\circ}$  for certain wave lengths. Thus a resolution of the asymmetric carbon atom has been effected giving rise to  $\ell$ -menthyl d.  $\beta$ -chloro  $\beta$  nitroso butyrate.

PART II.Rotatory Dispersion and Circular Dichroism of *l*-menthyl  
d /  $\Delta$  chloro /  $\Delta$  nitroso butyrate.

(This is the subject of a paper recently published in the Journal of the Chemical Society<sup>47</sup>).

The object in view was to determine the magnitudes of rotation and circular dichroism within an optically active nitroso band. With this attained, the contribution to the total rotation of the molecule due to the presence of the NO group can be calculated. This has been achieved for a few other compounds containing a chromophoric group (see Introduction) but this is the first occasion in which the NO chromophore has been successfully investigated.

Experimental. The preparation of the compound is described in Part I.

ABSORPTION. The absorption spectrum due to the nitroso group was examined photographically with a Spekker spectrophotometer, a 1 cm. column of a 0.0774 M. solution in alcohol being used.

It may be noted that very little work has been done on absorption spectra in this region of the visible spectrum. This has been principally due to the lack of suitable plates; infra red photographic plates have a region of minimum sensitivity between 6000 Å and 7000 Å. For the work done in



this section Ilford panchromatic plates were used. Unfortunately their sensitivity falls away beyond  $\lambda$  6500. It was necessary, therefore, to take observations on one plate for wave lengths up to about 6500 Å, with normal exposures, and to overexpose another plate to obtain readings between 6500 Å and 6900 Å.

Since using these panchromatic plates it was discovered that Ilford Long Range plates were admirably suited for absorption spectra work in the red end of the spectrum. With the slit of the spectrograph set at 3 divisions, a suitable exposure for the zero of the instrument was found to be 4 secs. using an 8 volt Filament Lamp as source. These plates record the continuous spectrum of the lamp right up to  $\lambda = 8200$  Å. Observations using different sources led to the conclusion that the best for line spectra in this region are the Co arc and the Hg arc.

With the Co arc set at about  $1\frac{1}{2}$  ft. distant from the slit of the spectrograph and the slit set at 4 divisions a full spectrum can be obtained extending to the line of wave-length  $\lambda$  8200. A 12 mins. exposure was given and then 20 mins. with a red glass filter inserted.

The Hg arc set at the same distance and the slit at 4 divisions gave a line spectrum up to the doublet, at  $\lambda$  8250. The exposure used was 1 min. and 20 mins. with the filter in. Use was made of these line spectra to

calibrate the scale of the spectrograph beyond the tested wave length of  $6700 \text{ \AA}$ . Although calculated theoretically the scale was found to be quite in order beyond this wave length and indeed up to  $\lambda$  8200.

Now, reverting to the actual absorption spectrum measurements using the panchromatic plates, the source used was a filament lamp run off 4 volts and the slit of the spectrograph set at 2 divisions. Exposure for the zero was  $\frac{1}{2}$  second. For wave lengths longer than  $6500 \text{ \AA}$  the lamp was run off 7 volts and longer exposures given.

To find a suitable concentration of solution the drum of the Spekker is set at the reading 1.5 and photographs taken with various concentrations of a 1 cm. layer until one is obtained in which the lower half of the spectrum is just darker than the upper half in the region of maximum absorption\*. The concentration required was found to be 2.24% in alcohol using a 1 cm. cell.

A series of photographs was then taken with drum readings from 0 to 1.5. Variation of exposures is calculated from the expression  $e = A \frac{t'}{t}$ , where A is a suitable exposure for the zero and  $\frac{t'}{t}$  is the antilog of the Spekker reading. The wave lengths at which the two contiguous spectra match are noted and a curve drawn, plotting wave length against molecular extinction coefficient, obtained from  $\epsilon = \frac{\text{Drum Reading}}{C \times l}$  where Drum Reading =  $\log \frac{I}{I_0}$

$C$  = concentration in gm. mols. per litre and  $l$  is the length of the column in cms.

Table 1 gives the absorption data obtained, and the absorption curve, which is seen to consist of two overlapping bands, is shown in fig.1 (full line).

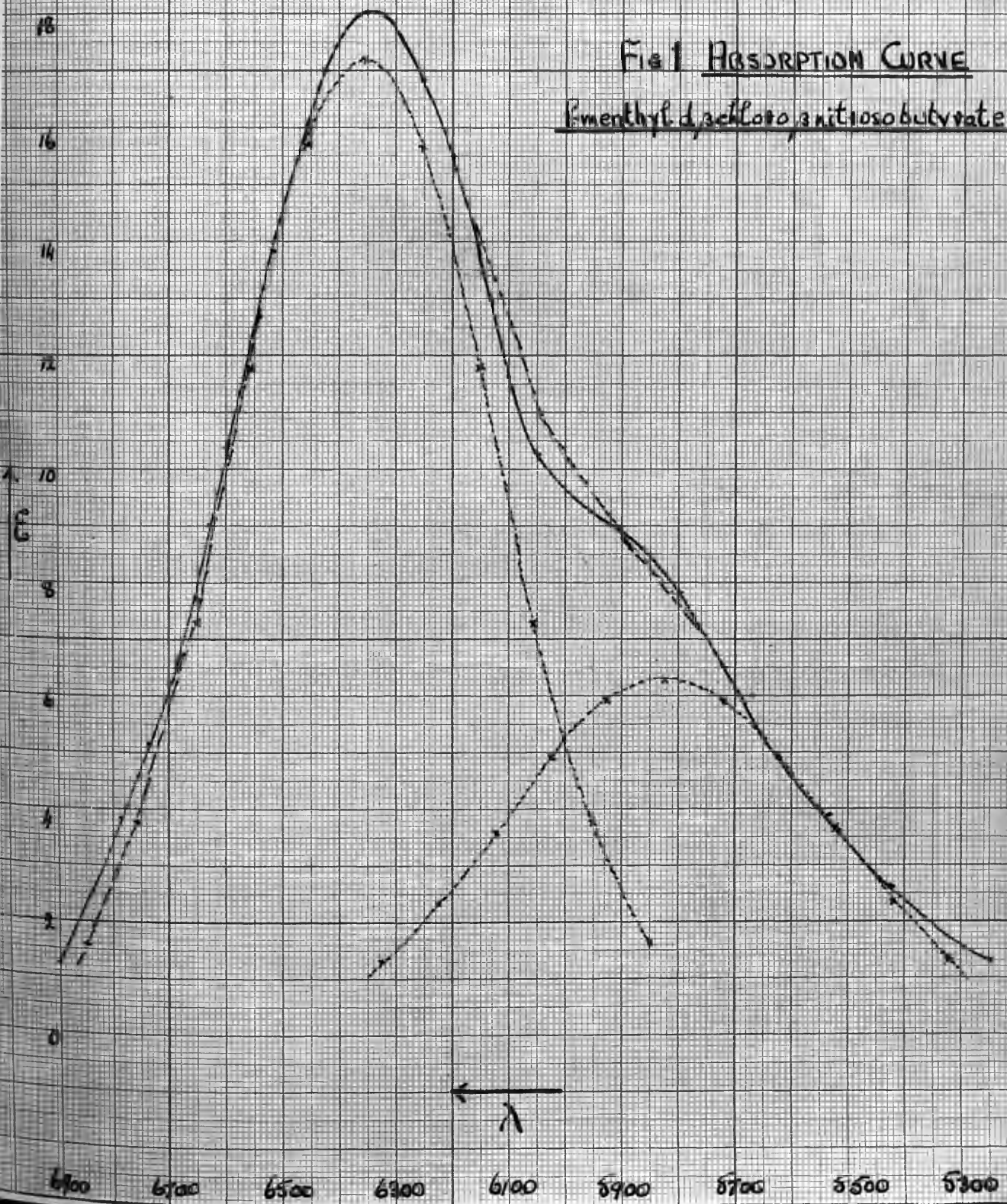
Maximum absorption occurs at  $\lambda$  6350 where  $\xi = 18.09$ .

600	0.1	0.1
610	0.2	0.2
620	0.4	0.4
630	0.8	0.8
640	1.5	1.5
650	2.5	2.5
660	3.5	3.5
670	4.5	4.5
680	5.5	5.5
690	6.5	6.5
700	7.5	7.5
710	8.5	8.5
720	9.5	9.5
730	10.5	10.5
740	11.5	11.5
750	12.5	12.5
760	13.5	13.5
770	14.5	14.5
780	15.5	15.5
790	16.5	16.5
800	17.5	17.5

Table 1.Absorption of *l*-menthyl d  $\beta$  chloro  $\beta$  nitroso butyrate.

$\lambda$	Drum Reading of Spekker.	$\epsilon$
5240	.1	1.29
5420	.2	2.59
5530	.3	3.88
5650	.4	5.17
5720	.5	6.47
5800	.6	7.76
5900	.7	9.05
6050	.8	10.34
6100	.9	11.64
6130	1.0	12.93
6160	1.1	14.22
6200	1.2	15.52
6250	1.3	16.81
6350	1.4	18.09
<hr/>		
6560	.9	11.64
6600	.8	10.34
6630	.7	9.05
6650	.6	7.76
6690	.5	6.47
6740	.4	5.17
6790	.3	3.88
6840	.2	2.59
6900	.1	1.29
<hr/>		

Fig 1 ABSORPTION CURVE  
(menthyl, d, 2-chloro, 3-nitrosobutyrate



### Rotatory Dispersion.

The rotation observations were made visually using a spectropolarimeter constructed from a Hilger polarimeter and Zeiss-Winkel monochromator. A 100 c.p. Pointolite lamp served as source. Readings taken at intervals between 6800 Å and 4800 Å are given in Table 2 and the rotatory dispersion curve shown in fig.3 (full line).

The concentration used was 0.6500 gm./100 c.c. in alcohol, and for wave lengths up to 6300 Å readings were taken in a 6 cm. tube. For readings inside the region of maximum absorption a 2 cm. tube was used. The temperature of the room during observations was 18°C.

For the full line curve in fig.3 it is obvious that the rotatory dispersion is anomalous. The curve rises to a negative maximum at  $\lambda$  5660 Å, where  $[\alpha] = -415.4^\circ$ . Thereafter the rotation curve shows a slight indentation due to the presence of the small overlapping absorption band. The rotation then falls steeply to zero at 6320 Å. This is approximately the wave length of maximum absorption recorded previously at 6350 Å. After crossing the zero axis the rotation rises steeply on the positive side and reaches a positive maximum of  $[\alpha] = 484.6^\circ$  at 6600 Å, thereafter only a few points could be accurately determined and they clearly show a descent on the other side of this maximum. The fact that the absorption spectrum is conveniently situated near the middle of the visible spectrum allows of readings to be taken through the absorption band showing the complete anomalous curve.

Table 2.

Rotatory Dispersion of *l*-menthyl $\alpha$ / $\beta$ chloro  $\beta$  nitroso  
butyrate.

(C = 0.6500 g./100 c.c.; t = 18°).

l = 6 cm.

$\lambda$	$\alpha$	$[\alpha]$
4800	-1.02°	-261.5°
4900	-1.07	-274.4
5000	-1.09	-279.5
5200	-1.17	-300.0
5400	-1.37	-351.3
5500	-1.47	-376.9
5600	-1.60	-410.2
5660	-1.62	-415.4
5700	-1.61	-412.8
5800	-1.51	-387.2
5900	-1.38	-353.8
6000	-1.33	-341.0
6100	-1.28	-328.2
6200	-1.05	-269.3
6300	-0.21	- 53.8

l = 2 cm.

6400	+0.28	+215.4
6500	+0.55	+423.2
6600	+0.63	+484.6
6700	+0.56	+430.8
6800	+0.46	+353.9

### Circular Dichroism.

Ellipticity readings were taken with the spectropolarimeter used for the rotation measurements but with a quarter-wave plate added behind the Lippich polarising system<sup>48</sup>. The rotation of the  $\frac{\lambda}{4}$  plate is controlled by a similar arrangement to the analyser fine adjustment in the polarimeter. Both regulating screws are provided with drums.

Described in the "Cotton Effect and Related Phenomena", Mitchell, the measurement of ellipticity in the visible is briefly as follows:-

- (1) An angle greater than the ellipticity to be measured is chosen for the half shadow angle.
  - (2) The analyser is adjusted to its zero position.
  - (3) The  $\frac{\lambda}{4}$  plate is introduced and oriented by the fine adjustment to maintain equal illumination.
  - (4) The  $\frac{\lambda}{4}$  plate is removed, the solution introduced and the rotation reading taken in the usual way.
  - (5) The  $\frac{\lambda}{4}$  plate is reintroduced and if the solution is circularly dichroic equality of illumination is destroyed.
  - (6) Equality of illumination is restored by turning both  $\frac{\lambda}{4}$  plate and the analyser in the same direction through the same angle. This angle is a measure of the ellipticity.
- Alkaline solutions of copper d-tartrate give negative ellipticities and this substance is convenient for determining the sign of the ellipticity to be measured by



comparison with the latter.

The actual angle obtained is converted to radians, ( $\tau$ ) and the difference in molecular extinction coefficients for right and left handed circularly polarised light is obtained from the equation (derived in the Introduction)

$$\frac{4. \tau \cdot 0.4343}{c \cdot l}$$

where  $\tau$  is angle in radians;  $c$  = concentration in gm. mols. per litre and  $l$  is the length of the column of solution in cms.

For the measurement of the circular dichroism of *l*-menthyl d 3 -chloro  $\beta$  nitroso butyrate a 0.6500% solution in alcohol was used with a 6 cm. tube for wave lengths between 5200 Å and 6100 Å. For wave lengths between 6200 Å and 6700 Å a 0.6440% solution was used in a 2 cm. tube, the temperature in both cases being 18°. A correction for the circular dichroism exhibited by the glass tube ends, due to slight strain, was experimentally observed and applied.

In Table 3 the above data is recorded. Figure 2 (full line) shows  $(\epsilon_e - \epsilon_r)$  graphed against wave length. This curve proves that the compound exhibits circular dichroism throughout the whole region of selective absorption. Indeed, the curve has an almost identical appearance to the absorption curve found for unpolarised light. The maximum in both cases occurs at 6350 Å and both show an effect due to an overlapping band.  $(\epsilon_e - \epsilon_r)_{\max} = +.67$ .

Table 3.

Circular Dichroism of  $\ell$ -menthyl  $d$   $\beta$  chloro  $\beta$  nitroso  
butyrate.

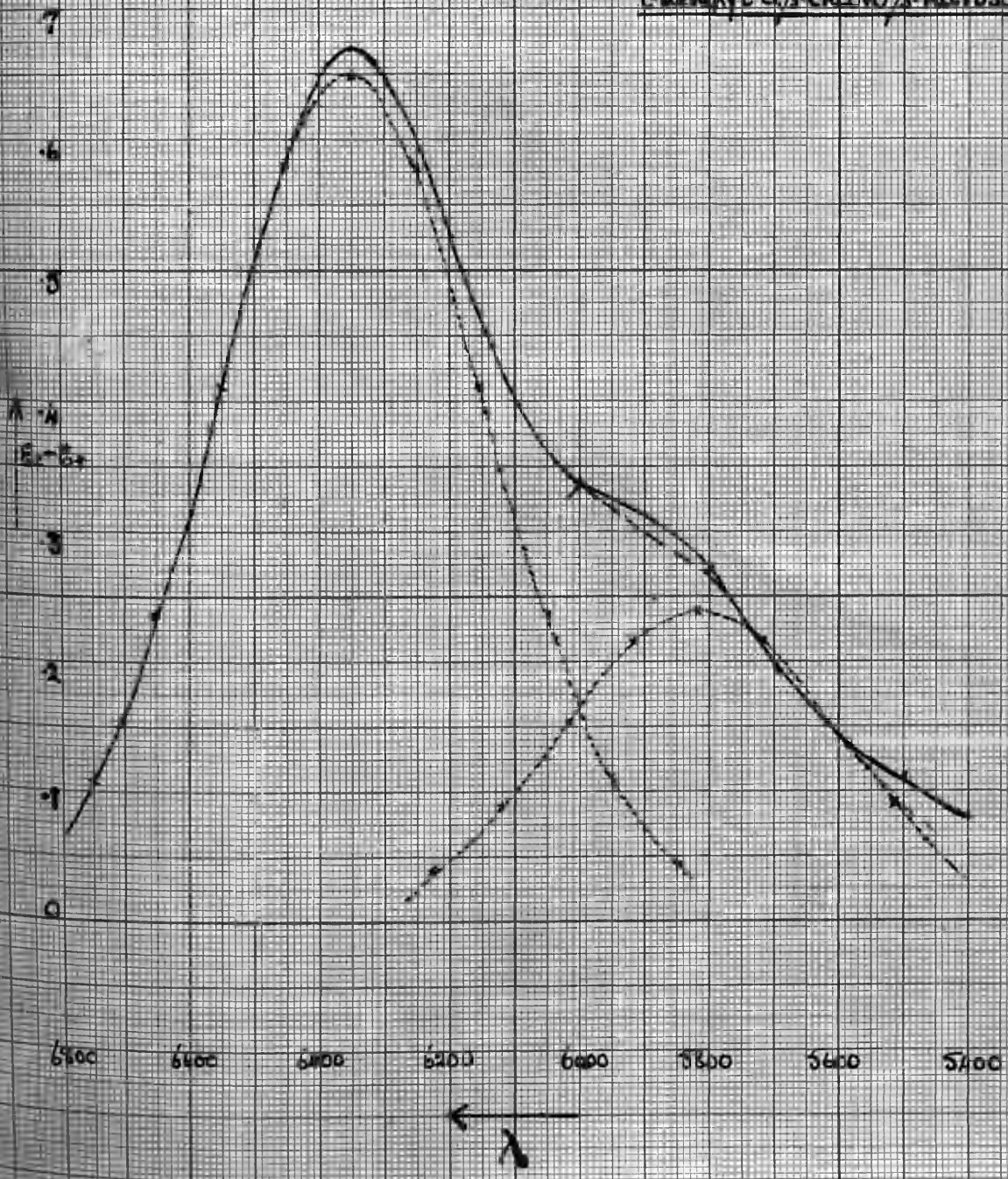
(Conc. .6500 g./100 c.c.;  $l = 6$  cm.;  $t = 18^\circ$ )

$\lambda$	Ellipticity	$\epsilon_2 - \epsilon_1$
5200	+0.27	+0.061
5400	+0.35	+0.079
5500	+0.51	+0.115
5600	+0.63	+0.142
5700	+0.86	+0.194
5800	+1.20	+0.270
5900	+1.48	+0.333
6000	+1.52	+0.342
6100	+1.75	+0.394

(Conc. .6440 g./100 c.c.;  $l = 2$  cms.;  $t = 18^\circ$ )

$\lambda$	Ellipticity	$\epsilon_2 - \epsilon_1$
6200	+0.77	+0.525
6300	+0.95	+0.648
6400	+0.95	+0.648
6500	+0.66	+0.450
6600	+0.45	+0.307
6700	+0.22	+0.150.

FIG. 2. CIRCULAR DICHROISM  
p-nonyl d,α-chloro-α-nitrosobutyrate



Mathematical Representation of Circular Dichroism and  
Absorption Curves.

As is fully explained in the Introduction, the partial rotation due to the optically active absorption band of a chromophoric group can be calculated if the position of the maximum and the half width of the curve of circular dichroism are known.

This task is not so simple in the present case for, as we have seen, the absorption system in the visible is composed of two overlapping bands.

Circular Dichroism Analysis.

By employing the equation

$$(\xi_{\ell} - \xi_{\tau}) = (\xi_{\ell} - \xi_{\tau})_{\max} e^{-\left(\frac{\lambda - \lambda_0}{\theta}\right)^2} \text{------(1)}$$

where  $\theta$  is a parameter embodying the half width of the band, it was found possible to analyse the curve of circular dichroism into two normal components. (See dotted curves in fig.2.).

To effect this analysis the positions of the maxima of the two components and the wave length at which  $(\xi_{\ell} - \xi_{\tau})$  is half the maximum value of the component curve are assumed, and by trial and error, the best fit for the observed curve is obtained after summing the two component curves.

Large Component Curve.

Assume  $\lambda_0$  (i.e) max. = 6350;  $(\xi_{\ell} - \xi_{\tau}) = .65$  (i.e.)  $\lambda - \lambda_0 = 250$   
 $\lambda = 6600 \text{ \AA}; (\xi_{\ell} - \xi_{\tau}) = .325$

∴ from equation (1) we have  $.325 = .65 e^{-\left(\frac{250}{\theta}\right)^2}$

which leads to the value 300 for parameter  $\theta$ .

Again, substituting in (1), we have

$$\log x = \log .65 - \left(\frac{D}{300}\right)^2 .4343$$

where D is the difference in wave lengths between the maximum and a point on the curve where the circular dichroism has value x.

x was then calculated for D = 100, 200, 300, 400, 500. These values are shown in Table 4(a) and when graphed give rise to the larger dotted curve in fig.2.

#### Small component Curve.

$$\left. \begin{array}{l} \text{Assume } \lambda_0 = 5820; (\xi_l - \xi_r)_{\max} = .24 \\ \lambda = 5570; (\xi_l - \xi_r) = .12 \end{array} \right\} \therefore \theta = 300$$

Results for this curve are given in Table 4(b) and the curve itself shown as a dotted line in fig.2.

It is seen from this graph that the agreement between the addition curve (broken line) and the experimental curve is very good.

#### Absorption Curve Analysis.

As above, the absorption curve was assumed to consist of two components of the type given by the equation

$$\xi = \xi_{\max} e^{-\left(\frac{\lambda - \lambda_0}{\theta}\right)^2}$$

For the large curve  $\lambda_0 = 6350; \xi_{\max} = 17.2; \theta = 324$

For the small curve  $\lambda_0 = 5820; \xi_{\max} = 6.35; \theta = 396$

Table 4.Analysis of Curve of Circular Dichroism.

Larger Component:  $\lambda_0 = 6350$ ;  $(\epsilon_l - \epsilon_r)_{\max} = .65$ ;  $\theta = 300$

$\lambda$	$\epsilon_l - \epsilon_r$
6350	.650
(6450)	.582
(6250)	
(6550)	.417
(6150)	
(6650)	.239
(6050)	
(6750)	.110
(5950)	
(6850)	.040
(5850)	

Smaller Component:  $\lambda_0 = 5820$ ;  $(\epsilon_l - \epsilon_r)_{\max} = .24$ ;  $\theta = 300$

$\lambda$	$\epsilon_l - \epsilon_r$
5820	.240
(5720)	.215
(5920)	
(5620)	.154
(6020)	
(5520)	.088
(6120)	
(5420)	.041
(6220)	
(5320)	.015
(6320)	

The results obtained from this equation are given in Table 5 and the graphs are shown as dotted curves in fig.1. The sum of these curves is represented by a broken line which again provides good agreement with the observed absorption curve.

Anisotropy Factor. Table 6 gives values of  $\xi$  and  $\xi_e - \xi_r$  obtained from each of the component curves for a number of wave lengths. From these the anisotropy factor  $(\xi_e - \xi_r)/\xi$  is calculated. It may be observed that in the middle of each band the factor has the same value (0.038) and remains fairly constant within the larger band but falls away from the maximum in the smaller band.

From the theoretical findings of Natanson it may be deduced that  $g = (\xi_e - \xi_r)/\xi$ , within an absorption band is proportional to the frequency. Thus, assuming this relationship the form of a circular dichroism curve can be ascertained from the related absorption curve and previous to the introduction of direct measurement of circular dichroism this method was used. The physical significance of the anisotropy factor<sup>49</sup>,  $g$ , is that it is that quantity by which the refractive index within an absorption band must be multiplied in order to obtain the circular dichroism and as Kuhn phrases it, "it is a measure of the activity of a band towards optical activity."

Table 5.Analysis of Absorption Curve.

Larger Component:  $\lambda_0 = 6350$ ;  $\xi_{\max} = 17.2$ ;  $\theta = 324$ .

$\lambda$	$\xi$
6350	17.2
(6450)	15.63
(6250)	
(6550)	11.75
(6150)	
(6650)	7.30
(6050)	
(6750)	3.74
(5950)	
(6850)	1.6
(5850)	

Smaller Component:  $\lambda_0 = 5820$ ;  $\xi_{\max} = 6.35$ ;  $\theta = 396$

$\lambda$	$\xi$
5820	6.35
(5720)	5.96
(5920)	
(5620)	4.92
(6020)	
(5520)	3.58
(6120)	
(5420)	2.30
(6220)	
(5320)	1.29.
(6320)	



Table 6.Anisotropy Factor.

<u>Large Band.</u>			
$\lambda$	$\epsilon$	$\epsilon_e - \epsilon_r$	$(\epsilon_e - \epsilon_r)/\epsilon$
5950	3.74	0.110	0.029
6050	7.30	0.239	0.033
6150	11.75	0.417	0.035
6250	15.63	0.582	0.037
6350	17.20	0.650	0.038
6450	15.63	0.582	0.037
6550	11.75	0.417	0.035
6650	7.30	0.239	0.033
6750	3.74	0.110	0.029
<u>Small Band.</u>			
$\lambda$	$\epsilon$	$\epsilon_e - \epsilon_r$	$(\epsilon_e - \epsilon_r)/\epsilon$
5420	2.30	0.041	0.018
5520	3.58	0.088	0.025
5620	4.92	0.154	0.031
5720	5.96	0.215	0.036
5820	6.35	0.240	0.038
5920	5.96	0.215	0.036
6020	4.92	0.154	0.031
6120	3.58	0.088	0.025
6220	2.30	0.041	0.018.

Resulting from the derivation of Kuhn's equation on the basis of a pair of coupled linear vibrators whose components are at right angles to one another and at a distance  $d$  apart, the relation  $d = \frac{g_{\text{max}} \lambda_0}{4\pi}$  can be deduced. Accounting for the fact that all the molecules do not possess the same orientation with respect to the incident light, the more general relation  $d = \frac{g \lambda}{2\pi}$  is obtained; "g" in this case is the average value of the anisotropy factor corresponding to wave length .

For an approximate evaluation of  $\underline{d}$  in the case under review let us apply the equation  $d = \frac{g_{\text{max}} \lambda_0}{4\pi}$  (i.e.) For the larger absorption band,

$$d = \frac{.038 \times 6350}{4\pi} = 1.992 \times 10^{-7}$$

and for the smaller

$$d = \frac{.038 \times 5820}{4\pi} = 1.761 \times 10^{-7}$$

These values are of intramolecular dimensions but consistent results for values of  $\underline{d}$  in other compounds cannot be obtained. To overcome this discrepancy Kuhn investigated a more general case of the two vibrator model in which the components are inclined at a small negative angle, and found that distances calculated on this basis are smaller than the linear dimensions of a molecule. Thus, he arrived at results which are physically possible but to which no clear meaning can be attached since it is unlikely that the hypothetical vibrator model gives an

accurate representation of the energy state within a molecule.

PARTIAL ROTATIONS DUE TO THE NO GROUP,

in  $\ell$ -menthyl  $\alpha$ -chloro  $\beta$ -nitroso butyrate.

The contributions to the rotatory dispersion curve associated with each of the component circular dichroism curves were calculated by means of the equation

$$[M] = \frac{100}{2\sqrt{\pi}} \cdot \frac{(\epsilon_e - \epsilon_r)_{\max}}{\log_{10} e} \cdot \frac{\lambda_0}{\lambda} \left[ e^{-\left(\frac{\lambda - \lambda_0}{\theta}\right)^2} \int \frac{\lambda - \lambda_0}{\theta} e^{x^2} dx + \frac{\theta}{2(\lambda + \lambda_0)} \right] \text{ in Rads.}$$

This is the Lowry and Hudson modification of Kuhn's equation, referred to in the Introduction. In fig.3, the partial rotation curves so obtained are shown as dotted lines and their sum is represented by the broken line. The method of calculation is as follows:

Converting the above equation to degrees and letting represent the terms inside the square brackets we have,

$$[M] = \frac{100}{2\sqrt{\pi}} \cdot \frac{57.296}{.4343} (\epsilon_e - \epsilon_r)_{\max} \frac{\lambda_0}{\lambda} \cdot m$$

$$\therefore [M] = 3723 (\epsilon_e - \epsilon_r)_{\max} \frac{\lambda_0}{\lambda} \cdot m$$

$$\therefore [\alpha] = 3723 \cdot \frac{100}{M} (\epsilon_e - \epsilon_r)_{\max} \frac{\lambda_0}{\lambda} \cdot m \quad \text{--- (A)}$$

where M = Molecular Weight of compound, i.e., M = 289.5

Large Component Curve of Circular Dichroism.

The maximum occurs at  $\lambda_0 = 6350$  where  $(\epsilon_e - \epsilon_r)_{\max} = .65$ .  $\theta = 300$ .

Substituting these values in equation (A)

we have

$$[\alpha] = 3723 \cdot \frac{100}{289.5} \cdot .65 \cdot 6350 \cdot \frac{m}{\lambda} \quad \text{--- (B)}$$

To obtain the values of  $\alpha$ , i.e., the value of the terms inside the bracket, corresponding to  $\lambda$  we proceed as follows:-

Six columns are headed as shown in Table 7.

Column 2 contains the values of C, i.e.  $\frac{\lambda - \lambda_0}{\theta}$  for which the value of the integral  $e^{-c^2} \int_0^c e^{x^2} dx$  can be obtained from the convergent series.

$$e^{-c^2} \int_0^c e^{x^2} dx = C - \frac{2C^3}{1.3} + \frac{2^2 C^5}{1.3.5} - \frac{2^3 C^7}{1.3.5.7} + \frac{2^4 C^9}{1.3.5.7.9} - \dots + \dots$$

These values are contained in column 3.

$$\text{Now, since } C = \frac{\lambda - \lambda_0}{\theta} \quad \therefore \quad \lambda = \lambda_0 + c\theta$$

$$\text{But } \theta = 300 \quad \therefore \quad \lambda = \lambda_0 + C.300$$

Therefore, for an increment of .1 in the value of C we have an interval in wave lengths of 30 Å.

Column 1 is composed of wave lengths at multiples of 30, different from  $\lambda_0$  at 6350 with the corresponding value of C in column 2.

Column 4 contains the values of  $\frac{\theta}{2(\lambda + \lambda_0)}$  and in column 5 the values of the complete integral are given for the corresponding wave lengths. Thus we now have a series of values for  $m$  and  $\lambda$  which can be substituted in equation (B) to give the desired rotations.

Small component curve.

$$\lambda_0 = 5820; (\epsilon_2 - \epsilon_1)_{\max} = .24; \theta = 300.$$

$$\therefore \text{we obtain } [\alpha] = \frac{3723 \cdot 100}{289.5} \left[ .24 \times 5820 \right] \cdot \frac{1}{\lambda}$$

Proceeding along similar lines to those outlined above, a set of partial rotations, due to the small band, are thus obtained and are given in Table 8.

When graphed, these partial rotation curves are summed to give the resultant partial rotation dispersion due to the optically active chromophoric nitroso group. The difference curve (thin full line) fig.3, obtained from this resultant and the experimental curve (heavy full line), represents the rotation of the molecule, the contribution of the NO bands being subtracted.

In few of the cases so far studied by other investigators has it been possible to eliminate so completely the anomaly due to a chromophoric group. This is no doubt due to the fact that such a satisfactory analysis of the composite band structure was effected, thus accounting for all anomalies. Previous examples of work of this type are given in the Introduction and also in Lowry's "Optical Rotatory Power." Most of the examples are concerned with only one component curve of circular dichroism, but in the case of octyl nitrite several bands are present.

Table 7.

Partial Rotations calculated from Large Component

Curve of Circular Dichroism.

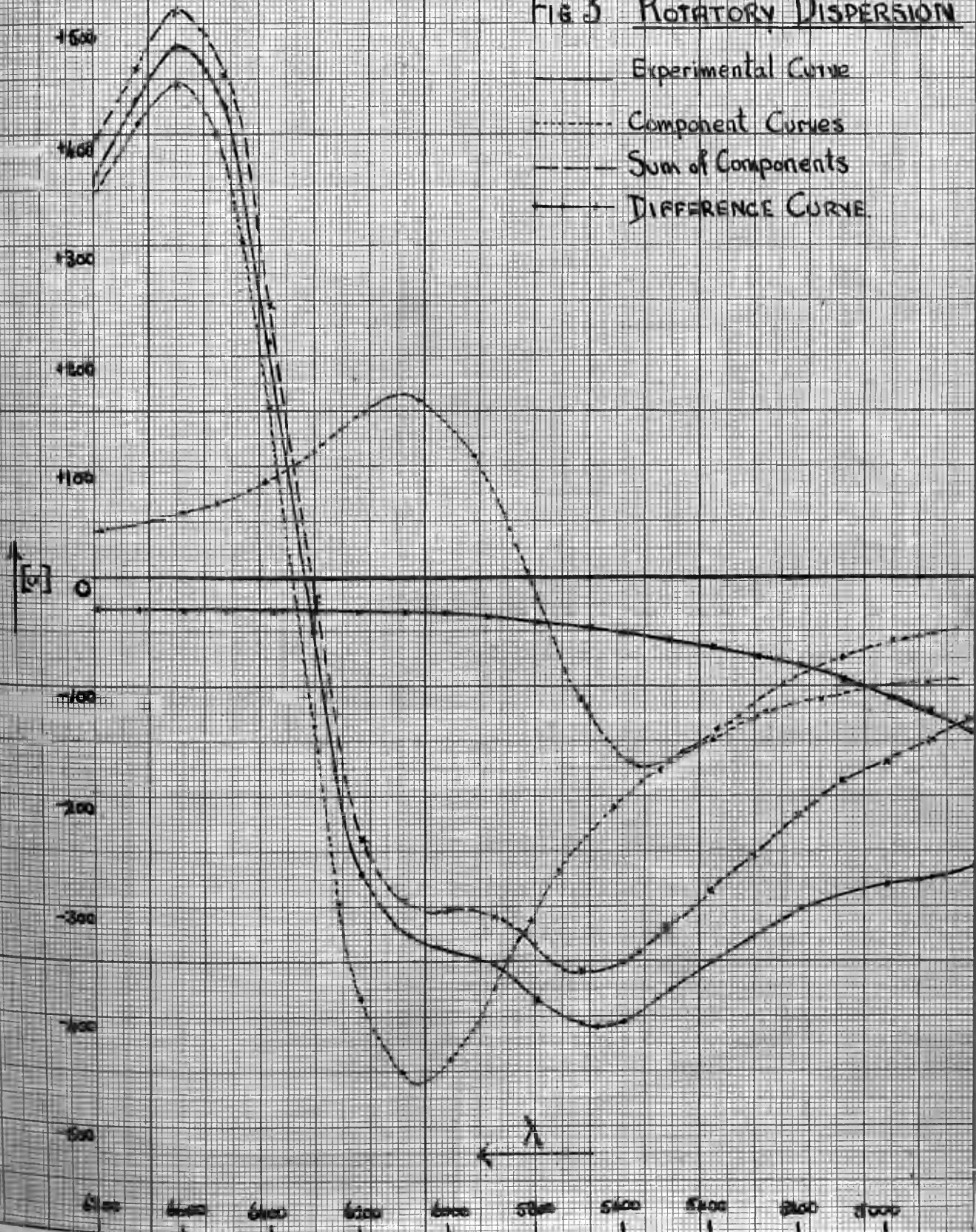
$\lambda$	$c$	$e^{-c^2} \int_0^c e^{x^2} dx$	$\frac{\theta}{2(\lambda+\lambda_0)}$	$m$	$[\alpha]$
6350	0.0	.00000	.01181	+.01181	+9.872
6470	+ .4	+.35943	.01172	.37116	304.5
6590	.8	.53210	.01160	.54370	437.9
6710	1.2	.50726	.01153	.51879	410.4
6800	1.5	.42820	.01143	.43963	344.7
6230	- .4	-.35943	.01192	-.34751	-296.0
6110	.8	.53210	.01208	.52002	451.7
5990	1.2	.50726	.01219	.49507	438.7
5870	1.6	.40000	.01227	.38773	350.5
5750	2.0	.30135	.01240	.28895	266.8
5630	2.4	.23530	.01255	.22275	210.0
5510	2.8	.19360	.01260	.18100	174.4
5390	3.2	.15630	.01280	.14350	141.3
5270	3.6	.13890	.01295	.12595	126.9
5150	4.0	.12500	.01305	.11195	115.4
5030	4.4	.11360	.01324	.10036	105.9
4910	4.8	.10420	.01332	.09088	98.24
4790	5.2	.09616	.01348	.08268	91.62

Table 8.

Partial Rotations calculated from Small  
Component Curve of Circular Dichroism.

$\lambda$	c	$e^{-c^2} \int_0^c e^{x^2} dx$	$\frac{\theta}{2(\lambda + \lambda_0)}$	m	$[\alpha]$
5820	0.0	.00000	.01290	+.01290	+ 3.98
5940	+0.4	+.35943	.01276	.37219	112.6
6060	0.8	.53210	.01263	.54473	161.4
6180	1.2	.50726	.01250	.51976	151.0
6300	1.6	.40000	.01238	.41238	117.6
6420	2.0	.30135	.01223	.31358	87.74
6540	2.4	.23530	.01217	.24747	67.98
6660	2.8	.19360	.01205	.20565	55.47
6780	3.2	.15680	.01194	.16874	44.7
5700	-0.4	-.35943	.01305	-.34638	-109.1
5580	0.8	.53210	.01318	.51892	167.0
5460	1.2	.50726	.01330	.49396	162.5
5340	1.6	.40000	.01348	.38652	130.0
5220	2.0	.30135	.01360	.28775	99.02
5100	2.4	.23530	.01373	.22157	78.05
4980	2.8	.19360	.01390	.17970	64.83
4860	3.2	.15680	.01410	.14270	52.74

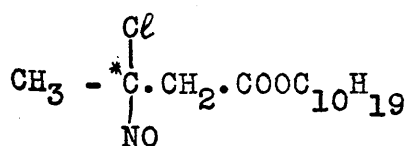
FIG 3 ROTATORY DISPERSION





The difference curve in this case, however, crosses the zero line several times. The residual curve in the case under review is very smooth and becomes increasingly negative with shorter wave lengths and bears out rather well the fact that the residual rotatory dispersion would be expected to behave in such a manner due to the presence of a laevo influence from the (-) menthyl group.

In this connection it may be noted that the crude (*d*) chloro nitroso ester shows very slight circular dichroism with a very low value maximum at  $\lambda$  6350 and no step out at  $\lambda$  5820. Thus, in the *dl* form of the ester there is perhaps an induced anisotropy due to the presence of a coupling of the absorption frequency of the chromophoric NO group in the field of fixed asymmetry due to the (-) menthyl radicle. On resolution of the asymmetric carbon atom to which is attached the NO and Cl groups the vicinal functions<sup>50</sup> of the neighbouring groups (CH<sub>3</sub>), (Cl) and (CH<sub>2</sub>COOC<sub>10</sub>H<sub>19</sub>) may begin to have effect with the result



that the circular dichroism and rotational magnitudes increase spectacularly. One of the

visible bands in the compound *l*-menthyl *d*  $\beta$  chloro  $\beta$  nitroso butyrate may thus be explained by the presence of the (-) menthyl group. A double band of similar type has been found by Mitchell and Cormack<sup>30</sup> to be present in bornylene nitrosite, whereas absorption bands due to the nitroso group<sup>67</sup>

in chloro nitroso derivatives of the paraffins studied by Cameron<sup>32</sup> have shown only one narrow absorption band as is the case with the absorption band of  $\gamma$  chloro  $\gamma$  nitroso valeric acid described in the next Part.

Note on the Mathematical Analysis of the Curve of Circular  
Dichroism.

The application of the empirical equation,

$$(\epsilon_c - \epsilon_r) = (\epsilon_c - \epsilon_r)_{\max} e^{-\left(\frac{\lambda - \lambda_0}{\theta}\right)^2}$$

to the curve of circular dichroism has already been described. This equation did not at first sight appear to be suitable for representing the curve in the case of the nitroso group, composed as it is of two components. Accordingly, an attempt was made to obtain a less empirical mathematical analysis using all the experimental data obtained in the circular dichroism observations.

Pearson<sup>51</sup> has evolved a method of analysing a curve into two normal frequency components but the method of calculation involves the solution of a ninth degree equation which, to say the least of it, is exceedingly laborious if not quite prohibitive. Recently, Charlier<sup>52</sup> has simplified the method of analysis by means of Pearson's nonic, by introducing three cubic equations.

These are:-

$$U_1 = -6v_3 u^3 + 3(v_5 - 10v_2 v_3) u^2 + 9v_3(v_4 - 3v_2^2) u + 6v_3^3$$

$$U_2 = 2u^3 + 3(v_4 - 3v_2^2) u + v_3^2$$

$$U_3 = 3u^3 + \frac{3}{2}(v_4 - 3v_2^2) u + \frac{2}{3} v_3^2$$

We now proposed to apply these for the first time to a curve of circular dichroism. From the experimentally observed data given in Table 3 and after lengthy

calculations the coefficients of these equations were evaluated.

The roots of  $U_2 = 0$  are now determined and the curves  $\omega' = \frac{U_1}{U_2}$  and  $\omega' = \pm \sqrt{U_3}$  are drawn. The point of intersection of these two curves gives a value for  $u$  and  $\omega'$ .

By substituting these values in the quadratic equation  $\gamma^2 - \frac{\omega}{u}\gamma + u = 0$ , the positions of the maxima of the two normal component curves can be obtained.

The values found were  $\lambda = 6384$  and  $\lambda = 5928$ .

Using these, a solution of the following equation can be effected:-

$$F(x) = \frac{N_1}{\sigma_1 \sqrt{2\pi}} e^{-\frac{(x-m_1)^2}{2\sigma_1^2}} + \frac{N_2}{\sigma_2 \sqrt{2\pi}} e^{-\frac{(x-m_2)^2}{2\sigma_2^2}}$$

The right hand side of this equation gives the two component curves thus:-

$$\varphi(x) = \frac{1}{\sqrt{2\pi}} e^{-\frac{x^2}{2}} \quad \text{Let } x = \frac{x-m_1}{\sigma_1}$$

$$\therefore \varphi = \frac{1}{\sqrt{2\pi}} e^{-\frac{(x-m_1)^2}{2\sigma_1^2}}$$

$$\therefore F(x) = \frac{N_1}{\sigma_1} \varphi_1 + \frac{N_2}{\sigma_2} \varphi_2$$

A table is made containing  $\lambda$ ,  $x$ ,  $\frac{x-m_1}{\sigma_1} \varphi_1$ ,  $\frac{N_1}{\sigma_1} \varphi$  and  $\frac{N_2}{\sigma_2} \varphi$ .

The value of  $\varphi$  corresponding to the value for  $\lambda$  can be found in the "Book of Tables for Statisticians and Biometricians". The values obtained for  $\frac{N_1}{\sigma_1} \varphi$  and  $\frac{N_2}{\sigma_2} \varphi$  are the points for the two component curves and the sum of

these respective values should give a curve similar to the original experimentally observed curve.

It was found, however, that curves so obtained did not give results so satisfactory as the final selection made by the trial and error method of Kuhn when the maximum positions of the two component curves are taken as

$$\lambda_1 = 6350 \quad \text{and} \quad \lambda_2 = 5820.$$

The results obtained above, by our absolute mathematical analysis are, however, reasonably close to the values finally used for the calculation of partial specific rotations from the circular dichroism data. The discrepancy of this absolute method may quite well be due to the fact that in the calculation of the coefficients of the cubic equations the largest moments used are those related to the least reliable observations, i.e., readings taken at  $\lambda = 5200$  and  $\lambda = 6700$ , etc., are not so accurate as those intermediate results and yet must be multiplied by larger amounts than the latter, so magnifying any experimental error.

A further simplification of this method of analysis was also tried<sup>52</sup>. It obviates the necessity for solving the cubic equations but entails the assumption of the maximum positions of the two curves. As such it does not differ materially from Kuhn's method which has itself the advantage of possessing some physical significance.

The computing involved in all the above calculations was done by means of a calculating machine kindly lent by Dr. R. Robb of the Mathematics Department.

PART III.Photochemical Decompositions and Measurements of Quantum Efficiencies.

Hammick and Lister<sup>53</sup>, in a photochemical investigation of some complex nitroso compounds, found that  $\beta$  chloro  $\beta$  nitroso  $\gamma\gamma$  dimethyl butane in presence of air was photo-oxidised to the nitro compound and in the absence of air the effect of light was negligible. In the case of chloro nitroso cyclohexane, photolysis occurred in the absence of oxygen but the decomposition products could not be identified. Traces of HCl and HNO<sub>2</sub> were claimed to have been detected but later work by Mitchell and Cameron<sup>32</sup> showed that the HCl liberated accounted for 95% of the total chlorine.

In a paper describing the preparation of chloro nitroso hexanes by the action of nitrosyl chloride on normal hexane under the influence of light, Mitchell and Carson<sup>34</sup> mention that chloro nitroso hexanes are decomposed by red light in the absence of air and that the hydrochlorides of methyl butyl and ethyl propyl ketoxime can be isolated. Much work has also been done by Mitchell and Cameron<sup>32</sup> on the photolysis of chloro nitroso compounds of the type  $R_1 - \begin{array}{c} \text{NO} \\ | \\ \text{C} \\ | \\ \text{Cl} \end{array} - R_2$  where  $R_1$  and  $R_2$  are simple alkyl groups.

They worked out, in particular, the photo-decomposition products of  $\beta$  chloro  $\beta$  nitroso butane,  $\beta$  chloro  $\beta$  nitroso propane and  $\beta$  chloro  $\beta$  nitroso hexane, both in the presence and absence of oxygen. In the photo-decomposition of the first of these compounds, in the absence of oxygen, the main compounds isolated were  $\text{HCl}$ , methyl ethyl ketoxime and diacetyl monoxime. For chloro nitroso propane those isolated were  $\text{HCl}$ , acetoxime and the monoxime of the ketonic aldehyde  $\text{CH}_3\text{COCHO}$ . In the case of chloro nitroso hexane, methyl butyl ketoxime and the monoxime of diketo hexane were detected in addition to  $\text{HCl}$ .

These decompositions were carried out using methyl alcohol, acetone, hexane and carbon tetrachloride as solvents and similar products obtained in each case, thus proving that the solvent plays no part in the photolysis.

Photodecomposition of  $\gamma$  chloro  $\gamma$  nitroso valeric acid  
in absence of Oxygen.

This decomposition was carried out in methyl alcohol, selected because it forms a homogeneous solution throughout the experiment.

A 5% solution of the blue acid was contained in sealed glass tubes kept cool by circulating water and illuminated by several metal filament lamps. On exposure to the light the solution paled in colour, turned green and then faintly yellow. On opening the tubes, the solution was found to be strongly acid due to hydrochloric acid.



The solvent was removed by evaporation under reduced pressure leaving a yellow oil. It was found that, by adding about four times the volume of dry ether to thin layers of this oil, a crystalline substance appeared after about ten minutes.

Product A. This crystalline substance was separated and washed with ether. It could be recrystallised from an alcohol-ether mixture. About 0.3 gm. of this compound was obtained from 3 gms. of the original chloro nitroso acid.

This product is very soluble in water, ethyl alcohol and acetone, but is insoluble in ether and benzene. It turns brown on exposure to the atmosphere but keeps well in a desiccator or in dry ether. The pure compound has m.p. 114°C.

Analysis.

Experimentally: C(39.71%); H(6.88%); N(7.7%); Cl(18.61%)

$C_6H_{12}NClO_3$  }  
requires: } C(39.67%); H(6.67%); N(7.7%); Cl(18.70%).

Thus, the empirical formula of the compound is  $C_6H_{12}NClO_3$  of molecular weight, 181.5.

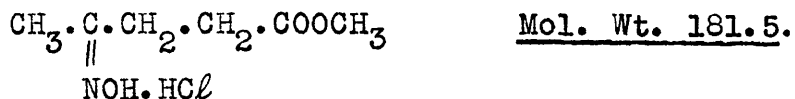
A molecular weight determination was made in ethyl alcohol by the elevation of the boiling point, using Menzies'<sup>54</sup> improved method involving the use of the differential thermometer. The value obtained was 181.9, which bears good agreement with the theoretical value of 181.5.

Constitution of Product A, C<sub>6</sub>H<sub>12</sub>NCℓO<sub>3</sub>.

(a) A solution of the photodecomposition product in water gives a precipitate with silver nitrate solution. This indicates the presence of chlorine in a hydrochloride and the latter explains the ready solubility in water and insolubility in dry ether.

(b) Chlorine gas passed through an aqueous solution with ether layer resulted in the production of a new blue substance which, when isolated, was found to distil under reduced pressure. The formation of this blue chloro nitroso compound indicates the presence of an oxime group in the compound. Since the original  $\gamma$  chloro  $\gamma$  nitroso valeric acid is non-distillable, it may be deduced that this blue compound is an ester. In the light of later results this compound must be methyl chloro nitroso valerate previously described in Part I. It would thus appear that the solvent, methyl alcohol, takes part to some extent in the photodecomposition reaction. This is certainly not without the bounds of possibility since methyl esters can form at moderate temperatures especially when catalysed by the presence of hydrochloric acid. In the case under review HCl is liberated at the outset and so paves the way for esterification to proceed.

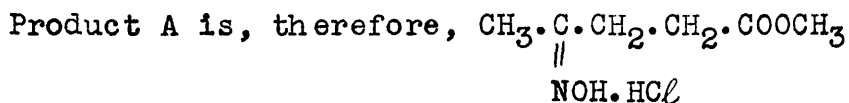
In view of the foregoing, the decomposition product A is probably the oxime hydrochloride of methyl laevulinate



Synthesis of oxime hydrochloride of methyl laevulinate.

The oxime of methyl laevulinate was prepared in the usual manner. Into a dry ethereal solution of the oxime dry gaseous HCl was passed and a white precipitate resulted. This solid was washed with ether and dried. It was re-crystallised from alcohol and ether. M.p. 115°.

A mixed melting point of the synthetic compound with product A of m.p. 114° showed no depression.



In order to isolate further products of the decomposition the following procedure was adopted:

After removal of the methyl alcohol a yellow oil remained. To this oil, as was described above, dry ether was added resulting in the precipitation of product A. The ethereal filtrate now obtained was used to isolate the remaining product or products.

Isolation of a second product.

The above ethereal filtrate was washed with cold dilute potassium hydroxide solution. The remaining ether solution was quite clear and on removal of the solvent a liquid residue was obtained. This liquid distilled almost entirely at 90°C/30 mms.

A 2:4 dinitrophenylhydrazine derivative was made. When recrystallised from alcohol it had m.p. 139°.

Analysis: C(46.53); H(4.52); N(17.64).

The 2:4 dinitrophenylhydrazone of methyl laevulinate of formula  $C_{12}H_{14}N_4O_6$  requires:-

C(46.45); H(4.52); N(18.06).

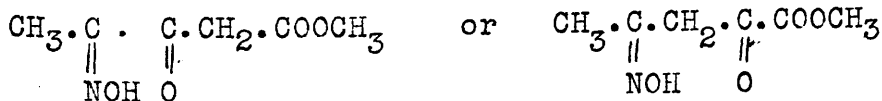
A semi-carbazone derivative gave the following analysis:-

C(45.23); H(6.95) and  $C_7H_{13}N_3O_3$  requires:-  
C(44.91); H(6.72).

A sample of methyl laevulinate was prepared and the 2:4 dinitrophenylhydrazine derivative was found to have m.p. 139°. A mixed melting point showed no depression.

Thus the second product obtained in the photodecomposition is methyl laevulinate,  $CH_3 \cdot CO \cdot CH_2 \cdot CH_2 \cdot COOCH_3$ , formed, no doubt, from Product A in the reaction tube.

The aqueous solution obtained after removal of these two products is quite red in colour and darkens considerably on standing or with slight heating. By analogy with previous work it was presumed that either the compound



is also formed in the photodecomposition. A red oil was isolated but attempts to distil or hydrolyse it led to decomposition and charring. No derivatives could be made and it is thought that complications had occurred due to internal condensation.

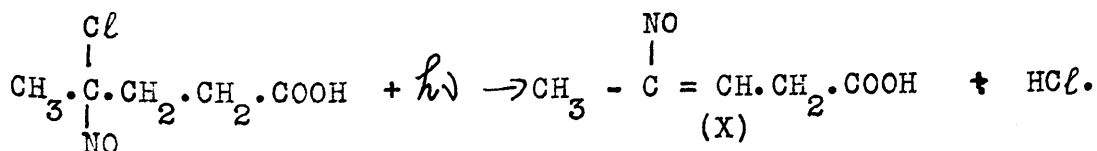
Estimation of hydrochloric acid liberated in the photolysis.

Samples of a 5% solution of the chloro nitroso acid were decomposed and the liberated hydrochloric acid estimated by titration with standard silver nitrate solution. The average percentage of Cl ion accounted for was 97.14 which is rather higher than that obtained for the chloro nitroso derivatives of the paraffins examined by Cameron<sup>32</sup>. This may be due to the fact that the chloro nitroso acid is a solid and can be obtained in a higher degree of purity than the liquids. This may also account for the fact that the quantum efficiency for the photodecomposition of the acid is nearer unity - this will be discussed later.

Reaction mechanism.

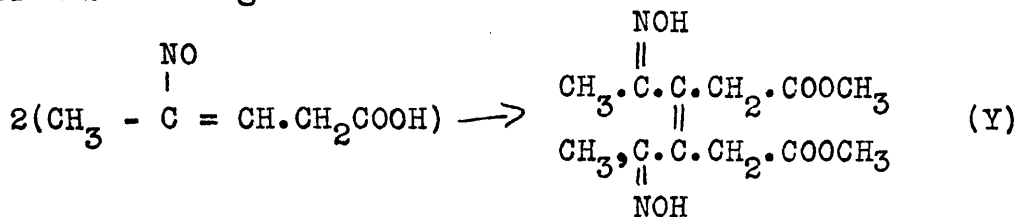
It is demonstrated below that the photodecomposition of chloro nitroso valeric acid obeys Einstein's Law of Photochemical Equivalence. This allows of a reaction mechanism similar to that used previously by Mitchell and Cameron.

During the photolysis, the energy absorbed by the nitroso group appears to pass to the adjacent carbon atom with the result that a <sup>proton</sup> ~~portion~~ is split off. Since Cl has a greater tendency to form a negative ion than NO, it is split off as HCl. The primary process is, therefore,

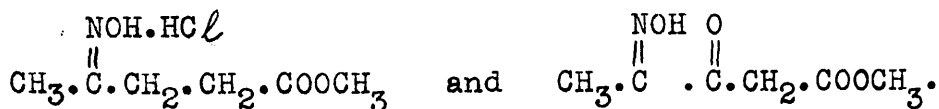


This is then followed by condensation of two molecules of

(X) which in the solvent, methyl alcohol, and in presence of  $\text{HCl}$  undergoes esterification



This then adds on  $\text{HCl}$  to give the monohydrochloride of (Y). The water liberated during the esterification causes a splitting resulting in the production of the compounds,



The first of these has been identified along with its oxime hydrolysis product, the free keto ester. The second compound could not be isolated.

#### Photodecomposition of menthyl chloro nitroso butyrate.

A 5% solution of this ester was exposed in sealed glass tubes to direct sunlight for about six hours. The solvent, methyl alcohol, was removed under reduced pressure and a reddish brown oil remained with a solid in suspension. The presence of  $\text{HCl}$  was detected. On neutralising and extracting with ether a yellow viscous oil was obtained. The presence of an oxime was detected and a vacuum distillation of the oil yielded an almost quantitative amount of menthol. This photodecomposition was not investigated further.

As a result of these photodecompositions it is important to record here the fact that the asymmetric centre of the original chloro nitroso compound has been destroyed.

### Measurement of the Quantum Yield.

The quantum theory of light requires that when a substance absorbs light one molecule only is changed by each absorbed quantum. This is the Photochemical Equivalence Law of Einstein. The number of molecules which react, however, as a result of the absorption of one light quantum may even be more or less than one according to the properties of the photoactivated molecule.

The quantity,  $\gamma$ , which may be experimentally determined is known as the Quantum Yield and is given by

$$\gamma = \frac{\text{Number of molecules reacting}}{\text{Number of quanta absorbed}}$$

From Einstein's generalisation of the quantum theory it was deduced that the amount of energy required to decompose one gram. molecule of photosensitive substance is  $Nh\nu$  ergs. =  $\frac{28470}{\lambda \text{ (microns)}}$  calcs. where  $\lambda$  is the wave length of light employed.  $h$  is the well known Planck constant.

$$\text{Thus } \gamma = \frac{\text{Molecules Decomposed}}{\text{Cals. absorbed}} \times \frac{2.847 \times 10^7}{\lambda \text{ (}\mu\text{)}}$$

Early experiments of Bodenstein<sup>55</sup> and Warburg<sup>56</sup> and many more carried out since have shown that the quantity can vary from small fractions to the value  $10^6$  observed for the hydrogen-chlorine reaction in the formation of HCl.

These departures from the Einstein Law are attributed to secondary chemical processes and do not detract from the validity of the fundamental principle which requires one quantum of light for the primary change.

Much the larger part of the work done in this field has been connected with decompositions involving the use of ultra violet light, but recently several measurements have been made with light from the red end of the spectrum. Briefly, these are referred to below.

The technique employed by Hoffmann<sup>57</sup> in determining the quantum yield for the photolysis with red light of caryophyllene nitrosite involved very long exposures due to the fact that the light source used was of very small intensity. The beam was rendered monochromatic by means of a spectrometer with further loss in light intensity. Recently, Anderson, Crumpler and Hammick<sup>58</sup>, and Hammick and Lister<sup>53</sup> have investigated the photochemical decompositions of some nitroso compounds and measured the quantum efficiencies of the reactions. As a result of the method used, exposure of the solution was of the order of 13 hours. The light employed for the decomposition was not monochromatic since they merely used filters which cut out infra red radiation.

Mitchell and Cameron<sup>32</sup> for the quantum yield measurements on some chloro nitroso compounds, developed a rather different technique from either of the above. The main



features of this method are the use of a source of sufficient intensity and the rendering of the resultant beam almost monochromatic.

In actual practice the light source employed is a carbon arc which is fairly rich in red light. The latter is made monochromatic by transmitting it through a Christiansen filter adjusted to a suitable temperature. During the experiment, variations in the intensity of the arc are recorded by reflecting a fraction of the light beam on to a Weston photronic cell connected to a recording galvanometer. The period of irradiation lasts 7 hours and the light is completely absorbed. Energy measurements are made by a thermopile-galvanometer system and the concentration measurements by means of a photo cell which replaces the thermopile.

Present Work.

Quantum Yield measurements for photolysis of  $\beta$  chloro  $\beta$  nitroso butane,  $\gamma$  chloro  $\gamma$  nitroso valeric acid and menthyl  $\beta$  chloro  $\beta$  nitroso butyrate.

The method we employed for these determinations was essentially that developed by Mitchell and Cameron and outlined above. Certain modifications were, however, effected and more sensitive instruments employed, with the result that the time of irradiation can be reduced.

In the original method the principal pieces of apparatus had been loaned by Professor F. Weigert when in the Department. On his departure, new apparatus had to be obtained and this provided an opportunity to increase the accuracy of the method. A large surface Moll thermopile and for use with it, a medium sensitivity Cambridge galvanometer were purchased. For measuring the change in concentration of the solution a high resistance Cambridge galvanometer was acquired for use with the photocell. With such sensitivity the percentage amount of decomposition does not require to be so great, thus allowing the period of exposure to be reduced to the convenient period of 4 hours.

In the arrangement described by Mitchell and Cameron a rectangular aperture of length 2.6 cms. was used. This aperture was replaced by a circular one of 2 cms., the diameter of the exposed part of the cell and of the thermopile being 1.8 cm. The circular apertures thus employed

in the optical train provide for the transmission of a more homogeneous beam of light from the cylindrical shaped Christiansen filter and are also more suitably adapted for use with the large surface thermopile.

Improvements were also effected on the thermostatic method for maintaining the Christiansen filter at a constant temperature below that of the room. The water in the thermostat was circulated, by pumping, through a cooling coil. A thermo-electric regulator used with a relay provided the necessary heating by means of an immersed silvered electric lamp. A minor change was also made in the photographic drum recording system. Previously the drum was rotated by clockwork using simply a friction drive, but in order to eliminate the possibility of the drum sticking, this was replaced by a lock-drive.

To test the new apparatus and modified method the quantum yield of  $\beta$ -chloro  $\beta$ -nitroso butane was measured. It was found to have the same value as that previously obtained by Mitchell and Cameron<sup>32</sup>.

Quantum Yield of  $\beta$ -chloro  $\beta$ -nitroso butane in methyl alcohol.

This compound was prepared by the action of chlorine on methyl ethyl ketoxime. It has b.p.  $35^{\circ}/50$  mms. The solvent used was methyl alcohol freed from oxygen. This compound possesses a narrow absorption band in the red with wave length of maximum absorption at  $\lambda$  6500: accordingly the thermostatic regulator was set to work at a temperature

of  $15.7^{\circ}$ .

### Calibration of Thermopile.

Gerlach<sup>59</sup> measured the energy radiated from a Hefner Lamp and found that the energy falling on an area of 1 sq. cm. at a distance of 1 metre from the lamp was  $2.25 \times 10^{-5}$  calcs. per sec. For the calibration of the thermopile in use a resistance of 50 ohms was placed in series with the galvanometer and retained for the duration of the quantum yield experiment. The usual precautions were taken and readings recorded at intervals of 10 secs. with the shutter alternately open and closed. "As the zero of the galvanometer shows a drift due to heating of the thermopile, the mean of two consecutive dark readings is taken as the zero for the 'light' reading which occurs between them." A typical set of results is given in Table 9.

### Experimental.

When the temperature of the thermostat had remained constant for half an hour, the carbon arc was switched on and a series of readings at 10 secs. interval taken on the thermopile while simultaneously the light falling on the photocell was recorded on the drum camera. The thermopile was then removed and the decomposition cell (an airtight cylindrical glass cell of vol. 4.03 ccs. with ground glass stopper) filled with a 7% solution of the chloronitroso compound in methyl alcohol was placed so that the aperture in front of it occupied the position just vacated by the

Table 9.Calibration of Thermopile.

Exposed surface 2.546 sq. cm.

Resistance 50 ohms.

Dark	Light	D
130	78	51.75
129.5	78	51.25
129	77.5	51.25
128.5	77	51.25
128	76.5	51.00
127	76	50.75
126.5	75.5	50.75
126	75	50.75
125.5	74	51.25
125	73	51.75
124.5	72	52.25
124		
		<u>Average 5.13 cm.</u>

thermopile. Since the opening of the thermopile is the same size as that of the cell holder the solution will receive the same amount of light as the thermopile, provided the intensity of the beam remains constant. Slight variations in this intensity during the period of irradiation were found from a record of the light falling on the photocell and knowing the ratio of the thermopile reading and the photocell reading, the amount of light falling on the solution can be calculated. At the end of four hours the cell was removed and 2 ccs. of the partly decomposed solution were taken and diluted to 6 ccs. with methyl alcohol. The arc was replaced by the projection lamp and the thermopile by the photocell. The diluted solution was placed in an open rectangular glass cell 1 cm. thick and placed before the photocell. The photocell was attached to the high resistance galvanometer and the scale reading noted. Similar readings were taken with the cell filled with solutions of known concentration. These solutions were made up by diluting the original 7% solution to various stages. Pipettes were used to deliver solution or solvent and a micro burette to extract a given volume of solution. It must be noted here that with the use of the highly sensitive photocell galvanometer arrangement the solutions, decomposed and original, require to be diluted only a third as compared with a fifth in the original method.

Calculation.

The thermopile has an exposed surface of 2.546 sq. cms., and it was employed with a galvanometer which, with 50 ohms resistance in series, gave a deflexion of 5.13 cms. on a scale at 100 cms. when the thermopile was exposed to the Hefner lamp at a distance of 1 metre.

∴ Energy per cm. per scale division per sec.  
 $= f = (2.25 \times 10^{-5} \times 2.546) / 5.13 \text{ cal} = 1.116 \times 10^{-5} \text{ cal}.$

Thermopile/Photocell Ratio.

T (cm.)	45.2	44.9	43.1	42.3	42.0
P (cm.)	8.2	8.2	8.2	8.1	8.1
$\frac{T}{P}$	5.5	5.5	5.4	5.3	5.2
T	47.7	47.8	46.7	45.0	
P	8.5	8.4	8.3	8.3	
$\frac{T}{P}$	5.6	5.7	5.7	5.4	

Average Ratio = 5.5.

For the actual irradiation 4 pairs of carbons each burning for about one hour were used. From the photographic record of the variations in the light intensity the mean photocell deflexion P' was found.

Carbons	Photocell Zero	Deflctn.	P'	Time
1	179	282	10.3	55 mins.
2	178	268	9.0	60 "
3	177	259	8.2	60 "
4	177	263	<u>8.6</u>	55 "
			Aver.	<u>9.03</u>

Allowing 5% correction for light losses by reflection we have:-

Total energy absorbed

$$= 1.116 \times 10^{-5} \times 5.5 \times 9.03 \times 1.05 \times 13,800 = 8.032 \text{ cal.}$$

Molecules Decomposed. Original Soltn. is 7.101%.

Concn. gms./100 ccs. Soltn.	2.367	2.170	1.973	1.578	x
Deflexion (cm.)	14.6	17.7	23.8	39.5	18.5

The concentration x of the partially decomposed solution (3 times diluted) was found graphically to be 2.145% ∴ concentration of decomposed solution before dilution is 3 x 2.145 = 6.435%.

$$\begin{aligned} \therefore \text{Gm. mols. decomposed} &= \frac{(7.101 - 6.435) \times 4.03}{100 \times 121.5} \\ &= \frac{.666 \times 4.03}{100 \times 121.5} \end{aligned}$$

$$\text{i.e. Gm.-mols. decomposed} = 2.21 \times 10^{-4}$$

Vol. of cell is 4.03<sub>ccs.</sub> and Mol.Wt. of compound is 121.5.

$$\therefore \text{Quantum Yield, } \chi = \frac{2.210 \times 10^{-4}}{8.032} \times \frac{2.847 \times 10^7}{650} = \underline{1.205}$$

Second Determination - see Table 10.  $\chi = \underline{1.227}$



Cameron<sup>32</sup> carried out experiments on the photodecomposition of  $\beta$ -chloro  $\beta$  nitroso butane in the light of certain influences. For example, he found that a solution of the compound had no appreciable dark reaction and that the decomposition was unaffected by the presence of HCl or concentration of the solution. He did find, however, that the quantum yield is increased by the presence of oxygen thus accounting for the precautions taken to ensure the elimination of oxygen from the methyl alcohol.

The results of these quantum yield determinations carried out by means of the new apparatus must be taken as being more accurate than those done hitherto. It is thus apparent that the photochemical decomposition of  $\beta$ -chloro  $\beta$  nitroso butane by light of wave length 6500Å in the absence of oxygen has a quantum yield of 1. This value admits of the reaction mechanism for the products of decomposition previously mentioned.

Now that the improved method had been tested and found to give comparatively good results, the Quantum Yields of  $\gamma$  chloro  $\gamma$  nitroso valeric acid and of menthyl chloro-nitroso butyrate were measured.

Quantum Yield of  $\gamma$  chloro  $\gamma$  nitroso valeric acid.

The absorption spectrum of this acid was measured in the visible by means of a Goldberg Spectrodensograph<sup>60</sup>. A cm. column of an approximately 1% solution in methyl

alcohol was used. The absorption curve is shown in fig.4 and possesses a maximum at  $\lambda$  6550,  $\epsilon = 20$ . To transmit this wavelength the temperature of the thermostat containing the Christiansen filter was regulated to remain constant at 15.4°C.

For the actual quantum yield measurement, a 7% solution of the acid in methyl alcohol, freed from oxygen, was used. The experimental details and calculation involved are exactly similar to those described above.

Tables 11 and 12 give the quantum yield determinations for  $\gamma$  chloro  $\gamma$  nitroso valeric acid.

The results are: (1)  $\gamma = 1.05$ , (2)  $\gamma = 1.10$ .

These values are lower than those obtained for the quantum yield of chloro nitroso butane. This may be explained by the fact that the solid acid can be obtained in a purer state than the liquid chloro nitroso butane. This statement, however, is not borne out by the quantum yield result for menthyl chloro nitroso butyrate which is also a solid and can be obtained very pure. The result in this case is  $\gamma = 1.19$  for the decomposition in acetone.

Quantum Yield of menthyl chloro nitroso butyrate.

The solvent used was acetone dried over anhydrous sodium sulphate and freed from oxygen. The absorption spectrum of this compound has already been fully discussed in Part II. The wave length of maximum absorption occurs at  $\lambda$  6350. The thermostat was accordingly maintained at

a temperature of 16.7°C.

To provide for complete absorption of the light a 15% solution in acetone was used. The results are given in Table 13.

In all the above photochemical decompositions it was found that a dark reaction was non-existent while the effect of HCl was quite negligible.

It has thus been clearly proved that these compounds possess a quantum yield of unity, i.e., only one molecule of the light sensitive compound is associated with each absorbed quantum of radiant energy. This result adds further weight to the theory of the mechanism of the reaction in the photolysis of  $\gamma$  chloro  $\gamma$  nitroso valeric acid in methyl alcohol. Although, in this case, the methyl alcohol takes part in the reaction, it does not interfere with the primary process, namely, the splitting off of a <sup>proton</sup>~~portion~~ from the carbon atom adjacent to the one to which the chlorine atom is attached.

FIG 4 ABSORPTION CURVE  
DEHLORO NITROSO VALERIC ACID

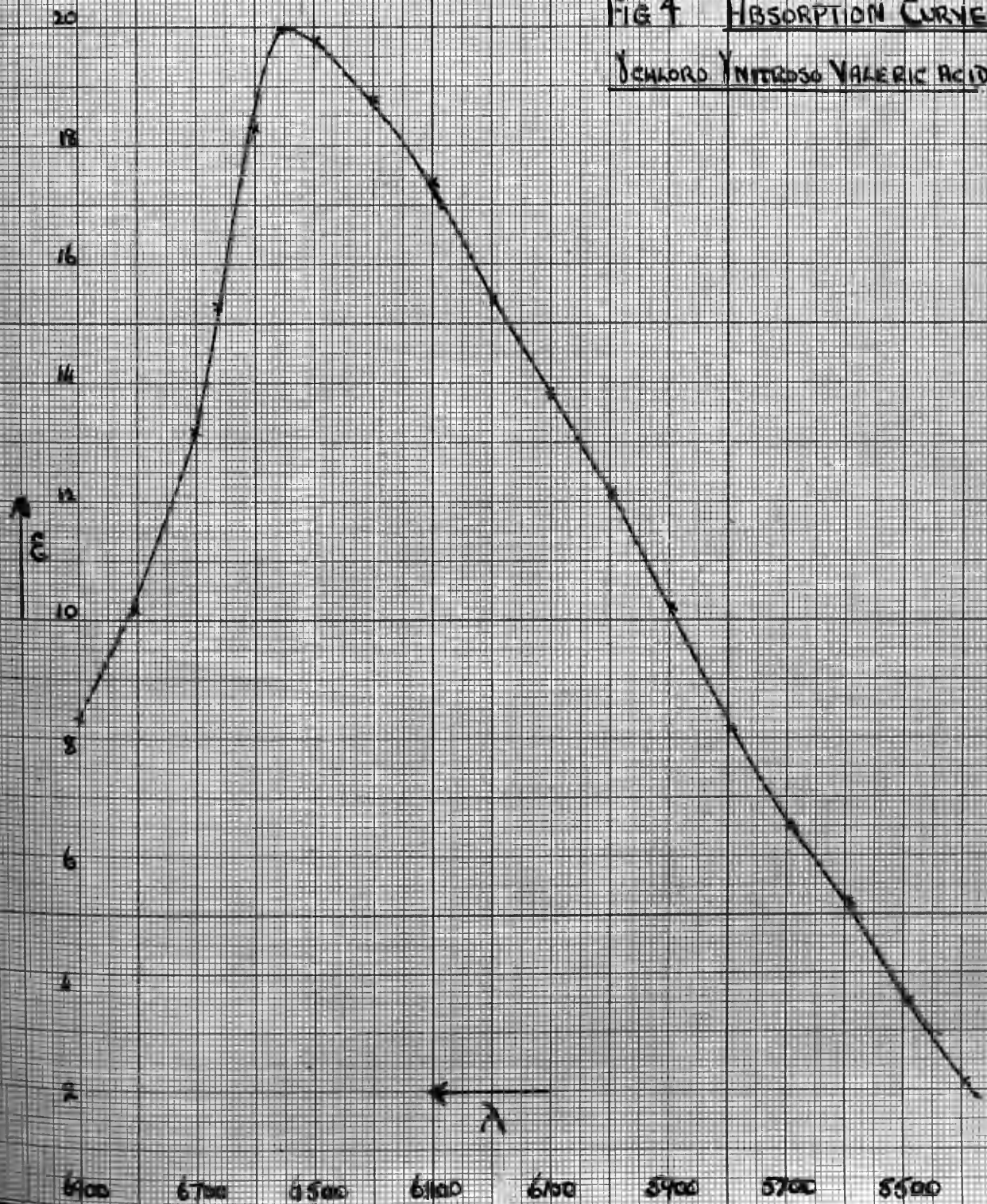


Table 10.Quantum Yield of 3 chloro 3 nitroso butane.Determination 2. Concentration 7.000%.

Concentration after irradiation 6.21%.

$$\therefore \text{Gm. mols. decomposed} = \frac{(7 - 6.21) \times 4.03}{100 \times 121.5} = 2.620 \times 10^{-4}$$

Average Photocell Deflexion .. .. 9.9 cm.

Ratio of Thermopile to Photocell, .. .. 5.6

Deflexion of Thermopile with Hefner Lamp .. 5.13 cm.

$$\therefore \text{Energy Absorbed} = 1.116 \times 10^{-5} \times 5.6 \times 9.9 \times 1.05 \times 14,400 \\ = 9.361 \text{ cal.}$$

$$\therefore \text{Quantum Yield, } \gamma = 1.227.$$

Table 11.Quantum Yield of  $\gamma$  chloro  $\gamma$  nitroso valeric acidAlcohol freed from oxygen.      Concentration 7%.

Conc. gms./100 ccs.	2.33	1.945	2.14	1.556	x
Photocell Deflectn.) with Projection Lamp	17.4	29.5	22.7	52.5	26.0

From Graph     $x = 2.03$ 

∴ Concentration of Decomposed Solution is 6.09%.

Initial Concentration                                    = 7%

Volume of Solution used                                 = 4.03 ccs.

$$\therefore \underline{\text{Gram Mols. Decomposed}} = \frac{(7 - 6.09) \times 4.03}{100 \times 165.5} = 2.216 \times 10^{-4}$$

Carbons	1	2	3	4	<u>Av.</u>	<u>Time</u>
Av. Photocell Deflection	9.8	8.8	8.5	8.5	8.9	4 hours

Ratio of Thermopile to Photocell Deflection = 6.1

Deflection on Thermopile with Hefner Lamp = 5.13 cm.

$$\therefore \underline{\text{Energy absorbed}} = 1.116 \times 10^{-5} \times 6.1 \times 8.9 \times 1.05 \times 14,400 \\ = 9.160 \text{ cal.}$$

$$\therefore \underline{\text{Quantum Yield, } \gamma} = 1.05.$$

Table 12.

Quantum Yield of  $\gamma$  chloro  $\gamma$  nitroso valeric acid.

Determination 2.Alcohol freed from oxygen.Concentration 7%.

Conc. gms./100 ccs.	2.33	1.945	2.14	1.556	x
Photocell Deflection with Projection Lamp	17.4	30.3	22.4	53	26.0

From Graph  $x = 2.05\%$ 

∴ Concentration of Decomposed Solution = 6.15%

Initial Concentration = 7%

Volume of Solution used = 4.03 ccs.

$$\therefore \underline{\text{Gram. Mols. Decomposed}} = \frac{(7 - 6.15) \times 4.03}{100 \times 165.5} = 2.069 \times 10^{-4}$$

Carbons	1	2	3	4	Av.	<u>Time</u>
Av. Photocell Deflection	10.3	9.95	9.8	10.8	10.22	4 hours.

Ratio: Thermopile/Photocell Deflection = 4.7

Deflection on Thermopile with Hefner Lamp = 5.13 cm.

$$\therefore \underline{\text{Energy Absorbed}} = 1.116 \times 10^{-5} \times 4.7 \times 10.22 \times 1.05 \times 14,400$$

$$= 8.104 \text{ cal.}$$

$$\therefore \underline{\text{Quantum Yield}}, \gamma = 1.1.$$

Table 13.Quantum Yield of Menthyl chloro nitroso butyrateAcetone freed from oxygen. Concentration 15%.

Concentration after irradiation = 13.8%.

$$\begin{aligned} \therefore \text{Gram Mols. Decomposed} &= \frac{(15 - 13.8) \times 4.03}{100 \times 289.5} \\ &= 1.67 \times 10^{-4}. \end{aligned}$$

Carbons	1	2	3	4	Av.	<u>Time</u>
Av. Photocell Deflection	7.4	6.8	7.9	7.6	7.43	13,260 secs.

Ratio of Thermopile/Photocell Deflection = 5.45

Deflection on Thermopile with Hefner Lamp = 5.13 cm.

$$\begin{aligned} \therefore \text{Energy Absorbed} &= 1.116 \times 10^{-5} \times 5.45 \times 7.43 \times 1.05 \times 13,260 \\ &= 6.291 \text{ cal.} \end{aligned}$$

$$\therefore \text{Quantum Yield, } \gamma = 1.19.$$



## DISCUSSION.

It has been indicated in the Introduction that the type of compound suitable for use in an asymmetric photochemical decomposition should possess somewhat specialised properties. In the light of data acquired for the chloro nitroso group of compounds, let us briefly review the position.

That an optically active form of one of these compounds exhibits the Cotton Effect within a spectral region has been demonstrated in the case of *l*-menthyl  $\underline{\alpha}$   $\beta$  chloro  $\beta$  nitroso butyrate. Such a compound has therefore the property of absorbing left and right handed circularly polarised light to different extents.

From this we have been able to determine the magnitude of the associated anisotropy factor. This factor, as has been explained, is a measure of the relative difference of absorption for the two kinds of circularly polarised light and the value obtained,  $g = .038$ , is above the average value obtained for other compounds. Cf. ethyl  $\alpha$  - bromopropionate,  $g = .024$ .

The fact that chloro nitroso compounds are chemically decomposed by the absorption of light of frequencies for which an active form exhibits circular dichroism, has also been more or less established. This is certain in the case of the above-mentioned menthyl ester and is most likely

to be true for chloro nitroso valeric acid and the other chloro nitroso compounds examined by Mitchell and Cameron, which are decomposed by red light.

In the last part of the thesis it has been shown that several such compounds have a Quantum Yield of unity for the photochemical reaction. For the chloro nitroso compounds studied by Cameron, this also holds. Thus, from a review of the products of photolysis it appears to amount to a general rule that all simple chloro nitroso compounds if and when decomposed by light give rise to products which are optically inactive and that the quantum efficiency for such photolyses may be regarded as being unity.

Kuhn<sup>61</sup> has evolved a formula which may be used to predict the value of the rotation which is developed by the decomposition of a racemic mixture with circularly polarised light.

It is,

$$\alpha' = \alpha \cdot \frac{g}{2} \cdot (1-\beta) \log \frac{1}{1-\beta}$$

where  $\alpha'$  = rotation developed from a solution of the 'dl' mixture,

$\alpha$  = corresponding rotation of a solution of the pure 'd' or 'l' form,

$g$  = anisotropy factor,

$\beta$  = degree of decomposition.

This relation holds only if the Einstein Photochemical Equivalence Law is obeyed in the photochemical reaction.

Thus, from a theoretical point of view we may apply it to the data obtained for the partial specific rotation calculated for the nitroso group in the case of *l*-menthyl  $\underline{d}$   $\beta$  chloro  $\beta$  nitroso butyrate.

In this case  $\alpha = 500^\circ (\lambda 6600\text{\AA})$  and  $g = .038$ .

Let  $\beta = 60\%$

then  $\alpha^d$  evaluates to  $3.48^\circ$ .

This result has little significance beyond indicating that the nitroso group would contribute some optical rotation to a compound if used in an asymmetric decomposition.

One drawback to the detection of a developed rotation by this means is the low concentration of the solution required to be used in the polarimetric reading on account of the rather strong absorption of the light by the blue solution. This can be partly offset by using a compound, the active form of which possesses a high specific rotation. It may also be suggested that for ease in observing any optical activity produced, the chloro nitroso compound remaining after irradiation could be oxidised to the chloro nitro compound. This oxidation can easily be effected in acetic acid solution by means of concentrated nitric acid, e.g., menthyl chloro nitro butyrate was prepared in this way and is a white solid which can be recrystallised from alcohol, m.p.  $81^\circ$ .

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S U M M A R Y.

In the earlier part of this thesis I have described the preparation of a number of new chloro nitroso compounds. Noteworthy among these are the three solid compounds  $\gamma$  chloro  $\gamma$  nitroso valeric acid,  $\alpha\alpha$  dimethyl  $\beta$  chloro  $\beta$ -nitroso butyric acid and menthyl  $\beta$  chloro  $\beta$  nitroso butyrate.

The first mentioned are the only two aliphatic nitroso acids known to exist in a stable monomeric form, while the last compound, when fully resolved, is the first case of optical activity in a chloro nitroso compound to be described.

In attempts to resolve chloro nitroso valeric acid by means of an optically active base or alkaloid, several crystalline blue salts were obtained, these being the salts with ephedrine alkaloid,  $\beta$ -naphthylphenylaminomethane,  $\alpha$ -phenyl ethylamine and *l*-menthylamine. The  $\alpha$ -phenylethylamine was prepared from acetophenone and resolved by means of quinic and tartaric acids, while the *l*-menthylamine was prepared from *l*-menthone as described in the literature. In spite of the fact that the salts could be recrystallised in splendid blue crystals from a suitable solvent, no optical activity could be detected in the liberated chloro nitroso acid.

With a resolution still in view, four menthyl and

two bornyl esters of some chloro nitroso acids were prepared. All these compounds were found to exist as heavy blue oils with the exception of *l*-menthyl chloro nitroso butyrate which is a blue crystalline solid. When subjected to several crystallisations from ethyl alcohol the melting point of this ester rises from  $58^{\circ}$  to  $71^{\circ}$ , while the specific rotation increases by about  $300^{\circ}$  for certain wave lengths, and circular dichroism is developed. It thus appears that a resolution of the asymmetric carbon atom has been effected giving rise to *l*-menthyl  $\alpha$  chloro  $\beta$  nitroso butyrate.

Part II of the thesis and J.C.S., 1940, 784 contain a full discussion of the rotatory dispersion and circular dichroism of this compound. The related absorption spectrum for unpolarised light (measured photographically using a Spekker Spectrophotometer) shows a double band in the visible due to the presence of the nitroso group and the curve obtained when circular dichroism is plotted against wave length has the same composite form. Each of these curves can be represented as the sum of two normal frequency curves and the anisotropy factors  $(\epsilon_2 - \epsilon_1)/\epsilon$  have the same maximum value of 0.038 for the corresponding components. Using the Lowry and Hudson modification of Kuhn's equation partial rotations were calculated for each of the circular dichroism components. When the sum of these is subtracted from the observed rotatory dispersion curve the difference

curve so obtained is relatively smooth.

Thus, the analysis of the composite band structure had successfully accounted for the anomalous rotation produced by the chromophoric nitroso group. This is the first time that the rotatory contribution of the optically active absorption system due to the NO group has been evaluated and may be regarded as a delicate test of the theoretical relation between optical rotatory power and circular dichroism.

In the last part of the thesis there is described the photochemical decomposition of  $\gamma$  chloro  $\gamma$  nitroso valeric acid in the absence of oxygen and using methyl alcohol as solvent. The products obtained are (1) HCl, (2) oxime hydrochloride of methyl laevulinate, (3) methyl laevulinate and a dark red oil which could not be identified. It was also ascertained that the compound, menthyl chloro nitroso butyrate, undergoes chemical decomposition on exposure to light.

A method of measuring quantum yields with red light was developed by Mitchell and Cameron. For work in this section certain modifications in the method were effected and more sensitive instruments employed. As a result of these alterations the period of irradiation of the solution can be reduced from seven to four hours and more accurate measurements made.

As a test, the quantum yield determination for the photolysis of  $\beta$  chloro  $\beta$  nitroso butane in methyl alcohol was made and found to be 1.2.

Following the measurement of the absorption spectra of  $\gamma$  chloro  $\gamma$  nitroso valeric acid and menthyl chloro nitroso butyrate, the quantum yield for these two substances was determined and the results  $\gamma = 1.1$  and  $\gamma = 1.2$ , respectively, obtained. In the former case the solvent used was methyl alcohol and in the latter, acetone.

All the important results obtained for these chloro nitroso compounds are correlated in the Discussion and there examined from the point of view of the suitability of these compounds for work on asymmetric photolysis. The conclusion arrived at is that such compounds fulfil the necessary conditions and appear to be suitable for this purpose.

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