

LVIII.—*Observations on the Influence of Temperature on the Optical Activity of Organic Liquids.*

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THAT the rotatory power of active substances is affected by temperature has been long known, but until recently few systematic experiments had been made in connection with this subject. In Landolt's well known monograph, *Das Optische Drehungsvermögen organischer Substanzen*, Brunswick, 1879, it is stated (p. 49) that as far as then known increase in temperature is most commonly accompanied by diminution in rotatory power, in support of which generalisation the experiments of Gernez on the specific rotation of some ethereal oils are cited. In these experiments, this diminution in rotatory power was studied between the temperatures of 0° and 150°. On the other hand, Landolt himself found (p. 69) that the specific rotation $[\alpha]_D$ of nicotine increased from 160·96° at 10·2° to 161·96° at 30°.

Similarly Pictet, subsequently Perkin, and more lately Freundler, have observed an increase in the rotatory power of the ethereal salts of tartaric acid with rise in temperature.

In our previous communications on the ethereal salts of glyceric and diacetylglyceric acids, we have incidentally drawn attention to the influence of temperature on their rotatory power, and have shown that whilst the rotation of both glycerates and diacetylglycerates is increased by rise of temperature, the latter are much more powerfully affected in this way than the former.

More recently we have had occasion to examine these changes in greater detail, and over wider ranges of temperature.

Effect of Temperature on Ethereal Salts of Glyceric acid.

Some months ago, Dr. Perkin kindly measured the magnetic rotation of two specimens of methylic glycerate, active and inactive, which we sent him, and on their return we were surprised to find that the rotation of the active methylic glycerate had undergone very material increase during the interval; thus, whereas it originally had $\alpha_D = -12.3^\circ$ (in the 198.4 m.m. tube), on its return the rotation was -14.82° at 18° , and -14.45° at 10° . We have recorded similar rises in the rotation of these ethereal glycerates in our first communication (Trans., 1893, 63, 523), and showed that they were due to partial decomposition taking place on long keeping at the ordinary temperature, but in this case the change had taken place in a much shorter time, namely, in less than three weeks. We were inclined to attribute this more rapid change to the fact that Dr. Perkin had made observations on this specimen at 35° , and that this comparatively high temperature had promoted the decomposition.

That the increased rotation was due to decomposition was distinctly proved by refractionating the specimen in a vacuum, when a considerable amount of non-volatile material was left (doubtless glyceric anhydride), whilst some distillate which was obtained at a low temperature was doubtless methylic alcohol, the main distillate being methylic glycerate, which now exhibited its normal rotation, namely, α_D (198.4 mm. tube) $= -12.6^\circ$ at 18° , and -12.1° at 11° . Thus, the increase in rotation caused by the decomposition is doubtless due to the formation of alcohol and glyceric anhydride, and the latter, as we have already shown, possesses a very high lævo-rotation; when the unaltered ethereal salt is separated from the non-volatile anhydride by distillation, it again exhibits the rotatory power originally observed.

As this decomposition is thus liable to occasion the most serious disturbances in the polarimetric observations, it obviously became necessary to further investigate the conditions under which it takes place. For this purpose, we employed two similar and freshly prepared specimens of ethylic glycerate, A and B. The part A, immediately after preparation, was cooled down to the lowest temperature we could command (4.9°), and at this temperature its rotation was first determined, and afterwards at temperatures rising to 35° , and then returning again to the low temperature. The portion B, on the other hand, was first examined at 35° , then at the low temperature, and then at temperatures rising again to 35° . The observed rotations in the 198.4 mm. tube under these conditions were as follows.

Ethylic Glycerate. Portion A.

| Temperature. | Observed rotation in 198·4 m.m. tube. α_D . | Date. | Remarks. |
|--------------|--|-----------|--|
| (1) 4·9° | -21·07° | 28.2.1894 | Rotation taken as soon as possible after preparation. |
| (2) 16·0 | -22·37 | 28.2.1894 | |
| (3) 35·0 | -23·43 | 1.3.1894 | |
| (4) 15·3 | -22·55 | 1.3.1894 | Kept at this temperature for 5½ hours before measurement was made. |
| (5) 4·8 | -22·15 | 2.3.1894 | |
| (6) 13·0 | -23·20 | 9.3.1894 | Had been kept at 35° for 24 hours previously. |
| (7) 5·2 | -22·90 | 10.3.1894 | |
| (8) 35·0 | -26·25 | 12.3.1894 | |
| (9) 35·0 | -26·15 | 13.3.1894 | Had been kept continuously at 35° since previous observation. |
| (10) 35·0 | -26·65 | 16.3.1894 | Had been heated in interval at 100° for 3 hours; during the remainder of the time it was kept at 35°. |
| — | — | 17.3.1894 | Had become quite turbid through separation of white flocculent material, doubtless glyceric anhydride. |

Ethylic Glycerate. Portion B.

| Temperature. | Observed rotation in 198·4 m.m. tube. α_D . | Date. | Remarks. |
|--------------|--|----------|---|
| (1) 35·0° | -23·50 | 3.3.1894 | Prepared on 2.3.1894, and kept for 3 hours at 35° before measurement. |
| (2) 4·8 | -22·27 | 5.3.1894 | |
| (3) 13·5 | -22·77 | " | Kept for 7 hours at 35°. |
| (4) 35·0 | -24·05 | 6.3.1894 | |
| (5) 35·0 | -25·35 | 7.3.1894 | Had been kept at 35° since previous observation. |
| (6) 13·3 | -23·45 | 8.3.1894 | No anhydride had separated, but product was becoming slightly yellow. |

These two series of observations show the necessity of exercising the greatest caution in drawing conclusions as to the effect of temperature on rotatory power. Thus, taking the first three observations on Portion A by themselves, it would appear that the rotation was extremely susceptible to temperature, an increase of 2·36° having taken place for a rise of 30° in temperature, but from the observations which follow it is obvious that this increase is largely due to decomposition, the rotation having become permanently raised for all temperatures. Thus also a very materially different rotation for

any particular temperature, say $4\cdot8^{\circ}$, will be obtained, according as the observation is at once made at this temperature, or only after observations have been previously made at higher temperatures. As it has been our invariable practice to determine the rotations of our ethereal salts at average air-temperatures, that is about 12 – 18° , immediately after their preparation, this decomposition, which goes on but very slowly at such temperatures, has not materially affected the accuracy of the observations which we have recorded, nor the deductions which we have made from them concerning the relations between optical activity and chemical constitution.

The supposition that the increase in rotation which attends this decomposition is due to the formation of the highly laevorotatory glyceric anhydride, is supported by the circumstance that in the experiments made with the Portion A above, there was finally, when the rotation had reached its highest figure, actually a separation of what was almost certainly glyceric anhydride. In order to further test this interpretation of the decomposition, we acetylated these two portions of ethylic glycerate which had undergone the partial decomposition in question, and obtained ethylic diacetylglycerate of practically exactly the same activity and density as that which we had previously prepared from ethylic glycerate which had undergone no such decomposition, thus the rotation of the ethylic diacetylglycerate prepared from the decomposed specimen of ethylic glycerate above was

$$\alpha_D = -37\cdot22^{\circ} \text{ at } 14\cdot9^{\circ} \text{ in the } 198\cdot4 \text{ mm. tube,}$$

whilst that of the ethylic diacetylglycerate prepared from an undecomposed specimen was

$$\alpha_D = -37\cdot46^{\circ} \text{ at } 15^{\circ} \text{ in the } 198\cdot4 \text{ mm. tube.}$$

This of course clearly shows that the increased rotation of the specimen of ethylic glycerate in question was due to the presence in it of an active substance which does not yield a volatile compound by acetylation, and not to any change in the activity of the undecomposed ethylic glycerate itself.

Owing to the facility with which this decomposition takes place in the ethereal salts of glyceric acid at higher temperatures, it becomes of course impossible to make any accurate experiments on the direct influence of temperature on their rotatory power. An approximate estimate, however, of the effect of temperature may be arrived at firstly by making a series of observations *with falling temperature*; thus in the two series of observations A and B, recorded above, we may utilise the following measurements for this purpose

$$\begin{array}{l} \text{Observations} \left\{ \begin{array}{l} (3) \ 35\cdot0^{\circ} \text{ C.} - (4) \ 15\cdot3^{\circ} \text{ C.} = 0\cdot045^{\circ} \text{ per } 1^{\circ} \text{ C.} \\ \text{on} \quad \quad \quad \left\{ \begin{array}{l} (4) \ 15\cdot3 \quad - (5) \ 4\cdot8 \quad = 0\cdot038 \quad \text{,,} \\ \text{Portion A.} \left\{ \begin{array}{l} (6) \ 13\cdot0 \quad - (7) \ 5\cdot2 \quad = 0\cdot038 \quad \text{,,} \end{array} \right. \end{array} \right. \end{array}$$

| | | | | |
|----------------------------------|---|-----------|-----------|--------------------|
| Observations on Portion B. | { | (1) 35.0° | —(2) 4.8° | = 0.041° per 1° C. |
| | | (5) 35.0 | —(6) 13.3 | = 0.087 „ |

Mean = 0.050° diminution in rotation per 1° C. fall in temperature.

The diminution in rotation thus arrived at for a fall of 1° in temperature is probably somewhat below the truth, as if any decomposition had taken place between two observations, it would render the later measurement at the lower temperature too high, and thus diminish the difference. On the other hand, by making a similar series of observations *with rising temperature*, figures will be obtained which are slightly above the truth, as any decomposition taking place between two observations would render the later measurement at the higher temperature too high, and thus increase the difference. Thus in the two series of observations A and B, recorded above, we may utilise for this purpose the measurements made on the rise (excluding, of course, those in which considerable intervals of time calculated to promote decomposition had elapsed).

| | | | | |
|---------------------------------------|---|-------------|---------------|--------------------|
| Observations made on Portion A. | { | (1) 4.9° C. | —(2) 16.0° C. | = 0.110° per 1° C. |
| | | (2) 16.0 | —(3) 35.0 | = 0.056 „ |
| | | (7) 5.2 | —(8) 35.0 | = 0.110 „ |

| | | | | |
|---------------------------------------|---|----------|------------|--------------------|
| Observations made on Portion B. | { | (2) 4.8° | —(3) 13.5° | = 0.057° per 1° C. |
| | | (3) 13.5 | —(4) 35.0 | = 0.059 „ |

Mean = 0.078° increase in rotation per 1° C. rise in temperature.

Thus the real increase in rotation for a rise of temperature of 1° C. must lie between 0.050° and 0.078°, but the fact that no less than three out of the five observations made with rising temperature are also but little above the lower figure, points to the latter being in all probability the nearer to the truth. (These figures have reference to the observed rotation α_D with the 198.4 mm. tube.)

Methylic Glycerate.—The measurements made by Dr. Perkin with this, when calculated for a tube of 198.4 mm. length, give—

$$\begin{aligned}\alpha_D &= -12.94^\circ \text{ at } 12.6^\circ \text{ C.} \\ &= -13.67 \text{ at } 21.0^\circ \text{ „} \\ &= -14.66 \text{ at } 33.0^\circ \text{ „}\end{aligned}$$

Mean increase = 0.085° per 1° C. rise in temperature.

This figure is, therefore, distinctly greater than that which we obtained for the ethylic glycerate above.

Influence of Temperature on the Rotatory Power of the Ethereal Salts of Diacetylgllyceric Acid.

As we have previously shown, these ethereal salts are much more stable than those of glyceric acid, and as the lower members, at any rate, can be distilled under atmospheric pressure without decomposition, and without change in rotatory power, they lend themselves better to the investigation of the influence of temperature on optical activity. In this connection, we have made a number of experiments with ethylic and octylic diacetylgllycerates respectively.

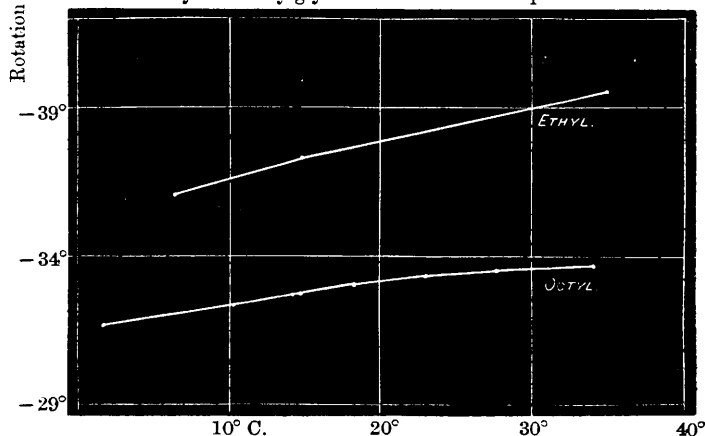
With ethylic diacetylgllycerate the following measurements were made.

| Temperature. | Observed rotation in 198.4 mm. tube. α_D . |
|--------------|--|
| 14.9° | -37.22° |
| 35.0 | -39.65 |
| 6.3 | -36.02 |
| 35.0 | -39.70 |

These figures show that the substance had undergone no permanent alteration in rotation during the course of the observations, and that the increment in rotation attending rise in temperature is, therefore, wholly attributable to the direct influence of temperature, and not to any decomposition, as was the case with ethylic glycerate.

The rotation of this ethylic diacetylgllycerate is, in fact, exceedingly sensitive to temperature, a rise of 1° in temperature being attended with a mean increase of 0.127° in the rotation observed in the 198.4 mm. tube.

Observed Rotation α_D in 198.4 mm. tube of ethylic diacetylgllycerate and octylic diacetylgllycerate at different temperatures.



The great regularity of this increase in rotation with the rise in temperature is exhibited by means of the diagram on p. 765, in which the abscissæ represent temperature and the ordinates the observed rotations.

With octylic diacetylgerate, the following measurements were made.

| Temperature. | Observed rotation in 198·4 mm. tube. α_D |
|--------------|--|
| 10·5° | — 32·40° |
| 35·0 | — 33·85 |
| 10·3 | — 32·40 |

Another series of observations gave the following results:—

| | |
|-------|----------|
| 10·1° | — 32·40° |
| 34·0 | — 33·82 |
| 23·0 | — 33·30 |
| 14·5 | — 32·77 |
| 18·0 | — 33·00 |
| 27·5 | — 33·55 |
| 1·4 | — 31·83 |

These figures again clearly show that during the period of the observations the rotation underwent no permanent alteration, and they further show that the rotation of octylic diacetylgerate is very considerably less sensitive to temperature than that of the ethylic compound, for the mean increment in rotation is only 0·062° for 1° rise in temperature in the case of the octylic, whereas it was 0·128°, or exactly double, in the case of the ethylic compound.

The great contrast in the sensitiveness to temperature of the rotation thus exhibited by ethylic and octylic diacetylgerates has led us to examine some of the other homologues in this respect.

Methylic Diacetylgerate.—In our previous communication, we have recorded the rotation of a specimen of this substance at two different temperatures.

$$\begin{aligned}\alpha_D &= -28·45^\circ \text{ at } 14^\circ \text{ in the } 198·4 \text{ mm. tube.} \\ &= -29·05 \text{ at } 17 \quad \quad \quad \text{,,} \quad \quad \quad \text{,,}\end{aligned}$$

These figures show an increase of no less than 0·20° for 1° C. rise in temperature, which is thus considerably in excess of the increase exhibited by ethylic diacetylgerate given above.

We have, therefore, made some further measurements over a wider range of temperature with another specimen, and have obtained the following figures.

$$\begin{aligned}\alpha_D &= -26·30^\circ \text{ at } 1·9^\circ \text{ in the } 198·4 \text{ mm. tube.} \\ &= -28·35 \text{ at } 13·5 \quad \quad \quad \text{,,} \quad \quad \quad \text{,,} \\ &= -31·30 \text{ at } 35·0 \quad \quad \quad \text{,,} \quad \quad \quad \text{,,} \\ \text{Mean increase} &= 0·155^\circ \text{ per } 1^\circ \text{ C.}\end{aligned}$$

Thus the figure obtained in these more accurate determinations is again markedly higher than that for ethylic diacetylgllycerate.

Normal Propylic Diacetylgllycerate.—We have made the following measurements with a specimen of this,

$$\alpha_D = -20.40^\circ \text{ at } 13.8^\circ \text{ in the } 99.2 \text{ mm. tube.}$$

$$= -20.60 \text{ at } 16.9 \quad \text{,,} \quad \text{,,}$$

$$= -20.77 \text{ at } 20.6 \quad \text{,,} \quad \text{,,}$$

from which the mean increase of 0.055° per 1° C. rise in temperature is obtained; but this figure must be multiplied by two in order to render it comparable with the others, as the observations were made in a tube of only half the length. The mean increase for the normal propylic compound is thus 0.11° per 1° C. , which is a little lower than that for the ethylic compound.

Isopropylic Diacetylgllycerate.—Several measurements at different temperatures were recorded by us in our previous communication, with specimens of different degrees of purity, thus the α_D in the 198.4 mm. tube was

| Specimen. | α_D . | Temp. | Increase per 1° C. |
|--------------|----------------------------|---------------------|-----------------------------------|
| No. 1..... { | -38.85° -39.25 | 14.0° 17.5 | } 0.11° |
| No. 2..... { | -38.10 -38.70 | 14.0 19.0 | |
| No. 3..... { | -39.95 -40.50 | 14.0 19.0 | } 0.11 |
| No. 4..... { | -40.15 -40.55 | 15.0 18.0 | |
| No. 5..... { | -39.08 -41.42 -37.60 | 13.9 35.0 1.9 | } 0.116 |

Although the several specimens were not all of quite the same degree of purity, yet the increase in all is very equal.

Isobutylic Diacetylgllycerate.—Of this we have only one pair of measurements on record, and, unfortunately, only in the shorter tube,

$$\alpha_D = -22.43^\circ \text{ at } 16.5^\circ \text{ in the } 99.2 \text{ mm. tube.}$$

$$= -22.73 \text{ at } 20.7 \quad \text{,,} \quad \text{,,}$$

$$\text{Increase} = (0.07 \times 2) = 0.14 \text{ per } 1^\circ \text{ C.}$$

As the above determinations were made over such a small range of temperature, we have repeated the measurements on another specimen, of which, however, we again had, unfortunately, only sufficient to fill the short tube; this specimen was not quite as pure as the

former one, but it is not probable that the influence of temperature would be much altered by this circumstance,

$$\alpha_D = -21.80^\circ \text{ at } 22^\circ \text{ C. in the } 99.2 \text{ mm. tube.}$$

$$= -21.50 \text{ at } 15^\circ \quad \quad \quad \text{,,} \quad \quad \quad \text{,,}$$

Increase in rotation $= 0.043 \times 2 = 0.086^\circ$ per 1° C. calculated on a 198.4 mm. tube.

Normal Heptylic Diacetylglycerate, in the 198.4 mm. tube.

| Specimen. | α_D | Temp. | Increase per 1° C. |
|------------|----------------------------|------------------------|-----------------------------------|
| No. 1..... | -34.55° -35.15 | 13.5° 19.0 | } 0.109° |
| No. 2..... | -17.15 -17.40 | 10.5 14.5 | |
| No. 3..... | -16.80 | 4.0 | } 0.105 |
| | -17.03 | 8.0 | |
| | -17.10 | 10.0 | |
| | -17.35 | 14.5 | |

Thus, altogether the mean increase $= 0.113$ per 1° C.

Collecting these results, the mean increase of rotation for a rise of 1° C. for the several ethereal salts of diacetyl glyceric acid is as follows.

| Ethereal salt. | Mean increase of α_D for the 198.4 mm. tube for 1° C. rise in temperature (between 0° and 35° C.). | Percentage increase in observed rotation for 1° C. rise in temperature. |
|--------------------------------------|---|---|
| Methylic diacetyl glycerate | 0.155° | 0.541 |
| Ethylic " | 0.127 | 0.339 |
| Propylic (norm.) diacetyl glycerate. | 0.110 | 0.253 |
| Isopropylic diacetyl glycerate..... | 0.116 | 0.291 |
| Isobutylic " | 0.086 | 0.193 |
| Heptylic (norm.) diacetyl glycerate. | 0.113 | 0.325 |
| Octylic " " | 0.062 | 0.189 |
| Methylic glycerate | 0.085 (calculated from de- terminations made by Dr. Perkin) | 0.692 |
| Ethylic glycerate | 0.064° (mean of measure- ments made with rising and with falling temperature) | 0.295 |

Thus, in both the above series of homologous compounds, the in-

crease in rotation for a given rise in temperature is greater for the methylic than for the ethylic compound, and in the diacetyl-series, which we have alone worked at in this connection for the higher members, the increase in rotation for the ethylic is greater than that exhibited by any of the higher homologues, the octylic compound showing the smallest increase of all.

In the table below we have also expressed this sensitiveness of the rotation to temperature, (1) as increase in specific rotation, (2) as increase in molecular rotation, and (3) as increase in molecular deviation, for 1° C. rise in temperature in each case, thus,

| | [α] _D . | | [M] _D . | | [δ] _D . | |
|-------------------------------------|---|-------------------------------------|--------------------|----------------------|-----------------------------|----------------------|
| | Increase for 1° C. rise in temperature. | Percentage increase for 1° C. rise. | Increase. | Percentage increase. | Increase. | Percentage increase. |
| Methylic glycerate | 0·355° | 0·74 | 0·043° | 0·75 | 0·200° | 0·72 |
| Ethylic „ | 0·033 | 0·36 | 0·045 | 0·37 | 0·166 | 0·31 |
| Methylic diacetyl-glycerate | 0·073 | 0·61 | 0·150 | 0·61 | 0·45 | 0·56 |
| Ethylic diacetyl-glycerate | 0·067 | 0·41 | 0·147 | 0·41 | 0·39 | 0·37 |
| Propylic (norm.) diacetyl-glycerate | 0·063 | 0·32 | 0·146 | 0·32 | 0·36 | 0·28 |
| Isopropylic diacetyl-glycerate | 0·065 | 0·36 | 0·152 | 0·36 | 0·37 | 0·31 |
| Isobutylic diacetyl-glycerate | 0·054 | 0·26 | 0·134 | 0·26 | 0·29 | 0·21 |
| Heptylic (norm.) diacetyl-glycerate | 0·067 | 0·40 | 0·194 | 0·40 | 0·40 | 0·35 |
| Octylic (norm.) diacetyl-glycerate | 0·043 | 0·27 | 0·128 | 0·27 | 0·23 | 0·21 |

From the above, it will be seen that the same relations are, in the main, preserved in each of these several methods of expression.

As far as we are aware, these are the first systematic observations made on an homologous series of this kind, excepting the following determinations, made by Pictet, on a few of the ethereal salts of tartaric acid, at the temperatures of 20° and 100° respectively.

Thus, in the case of these tartrates also, the increase in rotation exhibits a tendency to diminish in ascending the series, the increase in the case of the methylic being, however, smaller than in that of the ethylic compound. This irregularity, however, disappears if the percentage increase be calculated on the mean observed rotation, as in the last column above.

| Tartrate. | Observed rotation α_D calculated for a length of 200 mm. at | | Mean increase in rotation per rise of 1°C . | Percentage increase for rise of 1°C . |
|-----------------------|--|---------------|--|--|
| | 20° . | 100° . | | |
| Methylic | 5.69 | 14.98 | 0.116° | 2.04 |
| Ethylic | 18.47 | 29.97 | 0.144 | 0.78 |
| Propylic (norm.) | 28.22 | 36.23 | 0.100 | 0.35 |
| Isopropylic | 33.63 | 39.66 | 0.075 | 0.22 |

We have also expressed this sensitiveness to temperature of the rotation of the ethereal salts of tartaric acid in terms of the specific and molecular rotations, as well as of the molecular deviation, in just the same way as in the case of the glycerates and diacetylgllycerates above. Thus

| Tartrate. | $[\alpha]_D$. | | $[M]_D$. | | $[\delta]_D$. | |
|-----------------------|--|--|-----------|----------------------|----------------|----------------------|
| | Increase for 1°C . rise in temperature. | Percentage increase for 1°C . rise. | Increase. | Percentage increase. | Increase. | Percentage increase. |
| Methylic | 0.048° | 2.25 | 0.086° | 2.24 | 0.307° | 2.11 |
| Ethylic | 0.070 | 0.92 | 0.145 | 0.92 | 0.422 | 0.82 |
| Propylic (norm.) | 0.058 | 0.47 | 0.136 | 0.46 | 0.327 | 0.39 |
| Isopropylic | 0.049 | 0.33 | 0.115 | 0.33 | 0.257 | 0.26 |

Thus whilst the actual increase for the methylic tartrate is less than that for the ethylic, still the percentage increase for the methylic compound is much the greater, irrespectively of whether α_D , $[\alpha]_D$, $[M]_D$, or $[\delta]_D$ be considered.

Whilst the rotation of the ethereal salts of tartaric acid is thus very sensitive to temperature, that of the ethereal salts of diacetyl, dipropionyl, dibutyryl, &c., tartaric acids is said to be but little affected by temperature, and, in commenting on this phenomenon, Le Bel has recently (*Compt. rend.*, 118, 917) stated that "all the bodies with variable rotation actually known are simple ethers, that is to say, bodies in which the asymmetric carbon atom is only linked to a single radical containing an atom of oxygen linked to another radical; if, on the contrary, the asymmetric carbon atom is united to two radicals of similar constitution, the variations in power become almost

zero." . . . "It thus appears that the effect of two radicals of the same nature is compensated. It is thus intelligible why the series of the tetrasubstituted tartaric ethers behaves in such a regular manner." This generalisation is, however, quite out of harmony with the great sensitiveness to temperature of the ethereal salts of diacetyl glyceric acid, the effect of temperature on the rotation of which is in excess of that on the rotation of the simple glycerates.

It is very striking, that in each of these three series—glycerates, diacetyl glycerates, and tartrates—the greatest sensitiveness to temperature is met with in the case of those members in which an addition of CH_2 also produces the most marked effect on the rotation; or, in other words, in those cases in which the degree of molecular dissymmetry is most increased by a rise of temperature, the dissymmetry is also most increased by an addition of CH_2 , and *vice versa*. There is some probability, therefore, that after a certain point in such an homologous series of compounds has been reached, increase in temperature may actually be attended with a diminution in optical activity, since already at the heptylic compound for glyceric and diacetyl glyceric acids, the addition of CH_2 is, as we have shown, attended with a diminution in rotation.

In those cases in which we have made observations over the widest ranges of temperature, we find that there is an invariable tendency for the sensitiveness to temperature to be greater at the lower than at the higher temperatures. This phenomenon is still more marked in the case of measurements with several substances which have been recently made by Le Bel at temperatures down to -42° .

The results of our own experiments, as well as those of others, clearly show that the effect of temperature on optical activity will have to be more taken into consideration in the future than it has been in the past, and when systematically studied for a large number of active substances, it may assist in throwing light on the internal arrangement of the molecules of active compounds, for it has already been ascertained in several cases that the influence of temperature on rotation is independent of any molecular polymerisation. We are continuing these observations for other series of active compounds.
