

# LXIII.—*The Magnetic Rotation of Compounds supposed to contain Acetyl, or to be of Ketonic Origin.* Part II.

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I RECENTLY gave an account of the magnetic rotations of a variety of compounds of the kind referred to in the title of this paper (Trans., 1892, **61**, 800), many of which were shown to exist at ordinary temperatures partially or entirely in the tautomeric form, namely, as unsaturated hydroxylic compounds. Through the kindness of Professor Claisen I have been enabled to examine other substances of this class which he has discovered, and besides these, several methyl and ethyl derivatives of ethylic acetoacetate, the latter chiefly for the purposes of comparison. As the results have in several cases a close bearing on those recorded in the previous communication, the same heading is adopted, this being regarded as a second part of the investigation. As on the previous occasion, the experimental results are placed at the end of the paper.

### *Dimethylacetylacetone.*

In my previous paper I showed that monoketonic compounds gave normal magnetic rotations, whilst diketonic gave numbers showing them to be either mixtures of ketonic products with their unsaturated hydroxylic isomers, or as composed only of the latter; this was also found to be true of the triketonic compound diacetyl-

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acetone. But it was also noticed that the introduction of alcohol radicles conduced to the ordinary ketonic condition, acetylacetone being a hydroxy-compound, whilst its methyl- and ethyl derivatives were found to be mixtures of the ketonic and hydroxylic forms. It was, therefore, of interest to see what would be the effect of a further displacement of hydrogen by one of these radicles, and for this purpose, the beautifully crystalline dimethylacetylacetone was employed. On account of the results obtained with the first specimen used being at the time considered very remarkable, Professor Claisen very kindly prepared a second with special care, but this also gave similar numbers, as will be seen on referring to the experimental results. The following is a comparison of the rotation of this compound with the calculated value of acetylacetone as a ketonic compound. (Trans., 1892, **61**, 814.)

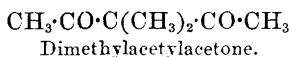
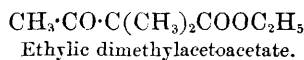
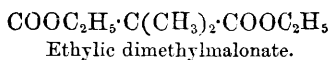
|  |       |
|--|-------|
| Mol. rotation of dimethylacetylacetone.... | 7.046 |
| „ acetylacetone (calc.) .....              | 5.553 |
| <hr/>                                      |       |
| 2CH <sub>3</sub> displacing 2H....         | 1.493 |

This difference is remarkably small, that ordinarily found for the change of composition = C<sub>2</sub>H<sub>4</sub> being 2.046, but, as pointed out in previous communications, the displacement of hydrogen by methyl sometimes gives a larger, and at other times a smaller alteration in rotation than is required by the change in composition. This latter result is especially noticed in the case of malonic derivatives, and from the results given in this paper it is seen to be also the case with acetoacetic compounds, thus:—

|                |                                     |       |         |
|----------------|-------------------------------------|-------|---------|
| Mol. rotation. | Ethylic malonate .....              | 7.410 | } 0.916 |
| „              | Ethylic methylmalonate ..           | 8.326 |         |
| „              | Ethylic dimethylmalonate .          | 9.268 |         |
|                | 2CH <sub>3</sub> displacing 2H..... | 1.858 | <hr/>   |
| Mol. rotation. | Methylic acetoacetate .....         | 5.376 | } 0.942 |
| „              | Methylic dimethylacetoacetate       | 7.133 |         |
|                | 2CH <sub>3</sub> displacing 2H....  | 1.757 |         |
| Mol. rotation. | Ethylic acetoacetate .....          | 6.501 | } 0.942 |
| „              | Ethylic dimethylacetoacetate ..     | 8.169 |         |
|                | 2CH <sub>3</sub> displacing 2H....  | 1.668 |         |

The differences found for the dimethylated malonic and acetoacetic compounds do not vary very greatly; they are, however, somewhat larger than that found in the case of dimethylacetylacetone. Nevertheless the differences are all of the same order, being less than

is required by the change of composition, and this is only what might be expected, as the methyl groups are all similarly related in these compounds, thus:—



From the foregoing, it is seen that the rotation of dimethylacetylacetone is not anomalous; it is also evident that it is a purely ketonic substance, the introduction of the second methyl into acetylacetone having entirely destroyed the tendency to pass over into the unsaturated hydroxylic isomer. The rotation of this compound was determined at temperatures widely apart, namely, at 19.3 and 92.3° but for the 73° difference, there was only a variation of 0.047, which is not more than might be expected for change of temperature alone.

From the rotation of dimethylacetylacetone, it is probable that the estimated values given in my previous paper for monomethyl-, and monethyl-acetylacetone in their ketonic conditions are a trifle too high, and if so, these substances at ordinary temperatures contain a somewhat larger amount of their hydroxylic isomers than is there stated.

#### *Allylacetylacetone.*

Having determined the rotation of the monomethyl and monethyl derivatives of acetylacetone, it was of interest to examine a derivative containing a different kind of radicle, and as Professor Claisen had furnished me with a specimen of allylacetylacetone, it was subjected to examination.

The rotation of allylacetylacetone as a ketonic compound may be estimated in the following manner

|   |       |       |
|---|-------|-------|
| Mol. rotation of acetylacetone (calc.)          | ....  | 5.553 |
| Allyl displacing H (as in allylic acetoacetate) | ..... | 3.881 |
|   |       | <hr/> |
|   |       | 9.434 |

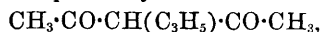
The molecular rotation found for this substance is, however, 10.597 at 15.75° or no less than 1.163 in excess of this calculation.

Its rotation as an unsaturated hydroxylic compound may be calculated from the corresponding saturated compound which would be acetylallylisopropyl alcohol

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|   |        |
|---|--------|
| Mol. rotation of acetoisopropyl alcohol (Trans.,<br>1892, p. 815) ..... | 5·777  |
| Allyl displacing H....  | 3·881  |
|   | <hr/>  |
|   | 9·658  |
| For unsaturation.....   | 1·112  |
|   | <hr/>  |
|   | 10·770 |

The rotation found is, therefore, only 0·173 lower than is required by the formula,  $\text{CH}_3\cdot\text{C}(\text{OH})\cdot\text{C}(\text{C}_2\text{H}_5)\cdot\text{CO}\cdot\text{CH}_3$ , but no less than 1·163 lower than that required by the formula



so that evidently it principally consists of the unsaturated hydroxylic compound at ordinary temperature.

The magnetic rotation was then determined at a considerably higher temperature than previously, to see if it changed to any important extent, like acetylacetone and its methyl and ethyl derivatives. At 95·6°, it was found to have fallen considerably, being then only 9·851, which is a reduction of 0·746 for a rise of 79·8°; at this temperature, therefore, its rotation only differs from that of the ketonic form of this substance by 0·417, of which, therefore, it chiefly consists.

As the behaviour of allylacetylacetone when heated is similar to that of methyl- and ethyl-acetylacetone (Trans., 1892, **61**, 817) in respect to rotation, it was of interest to see whether, after heating, it passed back to the ordinary, and principally hydroxylic condition, quickly, or only after the lapse of time, as was found to be the case with the above methyl compound.

To investigate this, a quantity of allylacetylacetone was introduced into a dilatometer provided with a second bulb near the top of the capillary tube, so that when heated there would be room for the expanded liquid. This was heated to above the top bulb about twenty minutes in the vapour of amyl alcohol, and then cooled to 15°. As soon as the level of the liquid became constant in the capillary tube, it was registered, and then examined at different intervals of time by placing it in water at 15°, and noting the position. There were considerable fluctuations in the atmospheric temperature during the progress of this experiment, which, probably, to some extent, affected the regularity of the changes observed. The following are the results obtained.

*Position after Heating and Cooling = 0·0 mm. at 15°.*

|                                |          |
|--------------------------------|----------|
| Resting during 22·0 hours..... | —3·5 mm. |
| “ “ 50·0 “ .....               | —10·0 “  |
| “ “ 71·0 “ .....               | —17·0 “  |
| “ “ 93·0 “ .....               | —21·0 “  |

A week after this, it was constant at  $-25.0$  mm. (the contraction had, however, probably ceased before the expiration of this last interval). To cause the product to regain the same volume it had, after being heated and then cooled to  $15^{\circ}$ , it was necessary to raise its temperature to  $19.75^{\circ}$ ; this would correspond to a change of density of about  $0.0032$  judging from the expansions of this substance. It therefore takes a very considerable time to get back again to a state of equilibrium after heating.

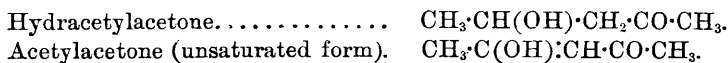
The refractive power of allylacetylacetone was also determined at two temperatures widely apart; the following are the results

|                                      | $t.$            | $\frac{\mu_A - 1}{d} p.$ | $\frac{\mu_F - 1}{d} p.$ | $\frac{\mu_G - 1}{d} p.$ | $\frac{\mu_H - 1}{d} p.$ |
|--------------------------------------|-----------------|--------------------------|--------------------------|--------------------------|--------------------------|
|                                      | $13.5^{\circ}$  | 66.16                    | 68.87                    | 70.25                    | 71.53                    |
|                                      | $99.2^{\circ}$  | 65.25                    | 67.64                    | 68.83                    | 69.94                    |
| Reduction owing to rise of temp..... | $85.7^{\circ}$  | 0.91                     | 1.23                     | 1.42                     | 1.59                     |
| For ..... ..                         | $100.0^{\circ}$ | 1.06                     | 1.44                     | 1.65                     | 1.85                     |

The calculated molecular refraction for the ketonic constitution for the line A is only  $63.5$ , but for the unsaturated hydroxylic constitution it is about  $65.8$ , only a little lower than that found. The dispersion equivalent is enormous, being about  $5.37$  for  $H-A$  at  $13.5^{\circ}$ , the reduction in dispersion caused by a rise of temperature of  $85.8^{\circ}$  above this, or to  $99.2^{\circ}$ , is also very considerable, amounting to about  $0.68$ . These results corroborate the magnetic rotations.

### *Hydracetylacetone.*

It has been shown (Trans., 1892, 813) that at ordinary temperatures acetylacetone has a very high rotation, showing that it is under those conditions an unsaturated compound, but that when heated to near the boiling point of water the rotation is considerably reduced, and it then consists of a mixture containing the unsaturated hydroxylic and the saturated ketonic compound. Since these results were published, Claisen has obtained the saturated compound corresponding to the unsaturated form of acetylacetone, namely, hydracetylacetone, by the condensation of acetone with aldehyde. The examination of this substance was of considerable interest, as calculated to confirm or disprove the conclusions previously arrived at and referred to above. The relationship of these products is as follows.



They therefore differ only by 2H, and consequently the rotations should vary to the extent usually found to exist between ordinary saturated and unsaturated substances.

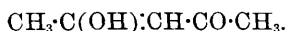
Hydracetylacetone may be regarded as an acetylisopropyl alcohol. The estimated rotation of this substance from this point of view, found from its series constants, has already been given (Trans., 1892, **61**, 815) as 5·777.

The actual rotation found was 5·871, which is only 0·094 higher than this estimate, and there is a possible explanation of this variation, which will be found further on.

On comparing the rotation of acetylacetone in its unsaturated form with this

|                                     |       |
|-------------------------------------|-------|
| Mol. rotation of acetylacetone..... | 7·166 |
| Hydracetylacetone ....              | 5·875 |
|                                     | <hr/> |
|                                     | 1·291 |

The average difference for unsaturation is 1·112, but in some cases it is higher, as between ethylic maleate and ethylic succinate where it amounts to 1·245, but as pointed out (Trans., 1892, **61**, 816) it is probable that the rotation of acetylacetone is a little high from the presence of a small quantity of a dihydroxy-compound, which would quite account for this difference being a little larger than usual; but be this as it may, the results are sufficiently close to confirm the conclusion that acetylacetone at ordinary temperatures practically consists of the unsaturated monhydroxylic compound



The rotation of hydracetylacetone was determined at two temperatures widely apart, namely at 14·9° and 95·1°; at the latter, the difference in the rotation was only 0·040 lower than at the former, an amount not greater than would be expected from change of temperature alone, and showing that it does not undergo any appreciable change of constitution under these circumstances, in this respect behaving very differently from acetylacetone.

The refractive power of hydracetylacetone was found to be for  $\frac{\mu_A - 1}{d} p$  44·16, the calculated number being 44·20. The dispersion equivalent for H—A was 2·02, the calculated 1·98; these numbers compare very well.

All the foregoing results show that hydracetylacetone is a saturated compound, agreeing with the constitution  $\text{CH}_3\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_3$ , such a substance might take the form  $\text{CH}_3\cdot\text{CH}(\text{OH})\cdot\text{CH}\cdot\text{C}(\text{OH})\cdot\text{CH}_3$ , and as the rotation found is a trifle higher than the calculated, it is

just possible it may contain a very small quantity of this isomer, which would influence the rotation in this manner.

*Ethylic Monocarboxyethylacetoacetate.*

I am indebted to Professor Claisen for a specimen of this substance, produced by the action of ethylic chlorocarbonate (chloroformate) on ethylic acetoacetate. B. p. 133° (11 mm.).

This substance can exist in two forms, thus—



These compounds are isomeric with ethylic acetonedicarboxylate, and the methods I employed to estimate the rotation of this substance (Trans., 1892, **61**, 813) will apply in this case also; for the saturated compound it was 9·444; but for the unsaturated isomer, 1·112 must be added to this, giving 10·556. The latter estimate, however, does not take into account the fact that the latter substance is of a type different from the saturated product, and unfortunately no analogous substance has yet been examined to compare it with. Considering it from the point of view of its being the representative of a carbonate and unsaturated ethereal salt, its rotation deduced from series constants would be 10·660.

Determinations of the rotation were made at two temperatures, and gave—

|                  |        |        |
|------------------|--------|--------|
| Mol. rotation at | 15·2°  | 10·401 |
| „                | 83·4°  | 10·181 |
|                  |        |        |
| Diff. for        | 68·2°  | 0·220  |
| „                | 100·0° | 0·322  |

It is seen from these results that this substance is not saturated; the rotation at the lower temperature, however, is not quite so high by 0·159 as the first estimate given for the unsaturated compound. It will also be seen that there is a considerable falling off in the rotation as the temperature increases, indicating that this causes it to modify to some extent and contain some of the saturated isomer, and in fact makes it probable that even at 15·2° it may contain a small quantity of this substance; this would account for its rotation being a little lower than the calculated number.

*Ethylic β-ethoxycrotonate.*

This beautifully crystalline substance was discovered by Freidrichs, who obtained it from chlorocrotonic acid: it has also been

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prepared from ethylic acetoacetate by Claisen, who has been good enough to let me have a specimen of the product from this source for examination. It fuses at  $31^{\circ}$ , and boils at  $199-200^{\circ}$ . It is isomeric with ethylic ethylacetoacetate.

The magnetic rotation was found to be  $10.430$ , whilst that of ethylic ethylacetoacetate is only  $8.329$  (Trans., 1892, **61**, 809), at once showing that it is an unsaturated compound.

The rotation of ethoxycrotonate may be estimated thus

|  |               |
|--|---------------|
| Mol. rotation of ethylic hydroxybutyrate |               |
| (calc. Trans., 1892, 805)                | 6.737         |
| „ ethyl displacing H as in               |               |
| ethyl oxide.....                         | 1.997         |
| „ Ethylic ethoxybutyrate                 | 8.734         |
| For unsaturation ..                      | 1.112         |
|  | <hr/> 9.846   |
| By series constants                      |               |
| Ethereal salt....                        | 0.337         |
| Ethylic oxide.....                       | 0.685         |
|  | <hr/> 2/1.022 |
|  | 0.511         |
| $\text{CH}_2 \times 8$ .....             | 8.184         |
|  | <hr/> 8.695*  |
| Ethylic ethoxybutyrate ....              | 1.112         |
| For unsaturation ..                      | <hr/> 9.807   |

The magnetic rotation of ethylic ethoxycrotonate is remarkable on account of its being so much higher than the calculated number, the difference being  $0.623$  in excess. It is, however, very interesting to notice that this amount is practically the same as is found in the case of ethylic fumarate, which is  $0.624$  higher than if it were an ordinary unsaturated compound (Trans., 1888, **55**, 593). The rotation of ethylic ethoxycrotonate thus shows that this substance is not only unsaturated but that it is also a *fumaroid*, corresponding to methylic  $\beta$ -methoxycoumarate, thus



\* Since writing this paper, the mol. rotation of ethylic ethoxybutyrate has been determined and found to be  $8.678$ .



The refractive power of this substance was also determined and found to be remarkably high, thus

| $t.$  | $\frac{\mu_A - 1}{d} p.$ | $\frac{\mu_H - 1}{d} p.$ | Disp. equiv.<br>H - A. |
|-------|--------------------------|--------------------------|------------------------|
| 32.4° | 71.43                    | 76.40                    | 4.97                   |

These numbers are considerably above those calculated for the unsaturated formula, the molecular refraction for A being only 68.3; this is also true of the dispersion equivalent, which should be only 3.13 instead of 4.97.

Dr. Gladstone found for ethylic fumarate at 7.5° for  $\mu_A$  1.4404, and for  $\mu_H$  1.4694; the molecular refraction calculated from these results gives

| $\frac{\mu_A - 1}{d} p.$ | $\frac{\mu_H - 1}{d} p.$ | Disp. H - A. |
|--------------------------|--------------------------|--------------|
| 71.13                    | 75.82                    | 4.69         |

The calculated values are only 69.1 for A and 3.54 for H - A, so that these results are closely analogous to those afforded by ethylic  $\beta$ -ethoxycrotonate, though the differences are not quite so large.

*Methylic Acetoacetate, Methylic Dimethylacetoacetate, Ethylic Dimethylacetoacetate, and Ethylic Diethylacetoacetate.*

With respect to methylic acetoacetate there is nothing special to note; its rotation is 1.125 lower than that of the ethylic salt; this is very similar to the difference existing between ethylic and methylic acetate, which is 1.100.

The peculiarities of the methylic and ethylic salts of dimethylacetoacetic acid have been already referred to in connection with dimethylacetoacetone, it being shown that the rotations they produce are similar to that of ethylic dimethylmalonate.

Ethylic diethylacetoacetate and also ethylic ethylacetoacetate when compared with ethylic acetoacetate, show differences similar to those found between the corresponding malonic compounds, though not following in quite the same order, thus

|  |        |         |
|--|--------|---------|
| Mol. rotation of ethylic acetoacetate..... | 6.501  | } 1.828 |
| "      "      ethylacetoacetate..          | 8.329  |         |
| "      "      diethylacetoacetate          | 10.115 |         |
|  |        | 3.614   |
| "      "      malonate.....                | 7.410  | } 1.862 |
| "      "      ethylmalonate....            | 9.272  |         |
| "      "      diethylmalonate ..           | 11.197 |         |
|  |        | 3.787   |

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The alteration in the rotation being less than that required by the change of composition, which for  $C_4H_8$  is 4.092

*Acetylacetone and Acetic Anhydride.*

In my previous paper (Trans., 1892, **61**, 836), when referring to the curious kind of equilibrium which exists between the proportions of acetylacetone in its two conditions, the ketonic and hydroxylic, at different temperatures, it was remarked that it would be interesting to examine it when mixed with another substance to see if this condition were disturbed by its presence. To test this, acetic anhydride was employed, molecular proportions of the two substances being taken, and the following results were obtained.

|                                |        |
|--------------------------------|--------|
| Mol. rotation of mixture ..... | 11.271 |
| „ acetic anhydride .....       | 4.284  |
| „ acetylacetone in mixture     | 6.987  |
| „ „ unmixed ..                 | 7.166  |
| Diff.....                      | 0.179  |

It is thus found that acetylacetone has a smaller rotation in this mixture than it has when alone, showing that the proportion of the ketonic product present has been increased, and therefore that the presence of acetic anhydride does influence it in this direction; but the influence is not very great, and not sufficient to account for the inactivity of the anhydride towards it when so large a quantity of the hydroxylic isomer is still present.

## EXPERIMENTAL RESULTS.

*Dimethylacetylacetone.*

| Spec. 1.         |         | Boiling point, 173—174°. |         | Density.           |         |
|------------------|---------|--------------------------|---------|--------------------|---------|
| <i>d</i> 15°/15° | 0.9564. | <i>d</i> 45°/45°         | 0.9381. | <i>d</i> 75°/75°   | 0.9241. |
| <i>d</i> 20°/20° | 0.9529. | <i>d</i> 50°/50°         | 0.9355. | <i>d</i> 80°/80°   | 0.9222. |
| <i>d</i> 25°/25° | 0.9497. | <i>d</i> 55°/55°         | 0.9329. | <i>d</i> 85°/85°   | 0.9204. |
| <i>d</i> 30°/30° | 0.9467. | <i>d</i> 60°/60°         | 0.9306. | <i>d</i> 90°/90°   | 0.9187. |
| <i>d</i> 35°/35° | 0.9438. | <i>d</i> 65°/65°         | 0.9284. | <i>d</i> 95°/95°   | 0.9172. |
| <i>d</i> 40°/40° | 0.9409. | <i>d</i> 70°/70°         | 0.9263. | <i>d</i> 100°/100° | 0.9158. |

The magnetic rotation once determined (40 readings) gave

| <i>t</i> . | Sp. rotation. | Mol. rotation. |
|------------|---------------|----------------|
| 19.35°     | 0.9442        | 7.042          |

At a higher temperature it gave (40 readings)

| <i>t</i> .                                  | Sp. rotation. | Mol. rotation. |
|---|---------------|----------------|
| 92.35°                                      | 0.9030        | 6.995          |
| Diff. for 73° = 0.047, or for 100° = 0.064. |               |                |

Spec. 2. Boiling point, 74—75° (16 mm.). Fusing point, 21°.

Density—

$d_{20^{\circ}/20^{\circ}}$  0.9584.  $d_{25^{\circ}/25^{\circ}}$  0.9550.  $d_{30^{\circ}/30^{\circ}}$  0.9520.

Magnetic rotation once determined (40 readings) gave

| <i>t.</i> | Sp. rotation. | Mol. rotation. |
|-----------|---------------|----------------|
| 20.8°     | 0.9498        | 7.051          |

Average of both specimens 7.046.

*Allylacetyl Acetone.*

Boiling point, 92° (16 mm.). Density.

|                                     |                                     |                                       |
|-------------------------------------|-------------------------------------|---------------------------------------|
| $d_{4^{\circ}/4^{\circ}}$ 0.9851.   | $d_{35^{\circ}/35^{\circ}}$ 0.9643. | $d_{70^{\circ}/70^{\circ}}$ 0.9478.   |
| $d_{5^{\circ}/5^{\circ}}$ 0.9843.   | $d_{40^{\circ}/40^{\circ}}$ 0.9637. | $d_{75^{\circ}/75^{\circ}}$ 0.9457.   |
| $d_{10^{\circ}/10^{\circ}}$ 0.9801. | $d_{45^{\circ}/45^{\circ}}$ 0.9592. | $d_{80^{\circ}/80^{\circ}}$ 0.9436.   |
| $d_{15^{\circ}/15^{\circ}}$ 0.9763. | $d_{50^{\circ}/50^{\circ}}$ 0.9568. | $d_{85^{\circ}/85^{\circ}}$ 0.9416.   |
| $d_{20^{\circ}/20^{\circ}}$ 0.9730. | $d_{55^{\circ}/55^{\circ}}$ 0.9544. | $d_{90^{\circ}/90^{\circ}}$ 0.9397.   |
| $d_{25^{\circ}/25^{\circ}}$ 0.9699. | $d_{60^{\circ}/60^{\circ}}$ 0.9521. | $d_{95^{\circ}/95^{\circ}}$ 0.9379.   |
| $d_{30^{\circ}/30^{\circ}}$ 0.9670. | $d_{65^{\circ}/65^{\circ}}$ 0.9499. | $d_{100^{\circ}/100^{\circ}}$ 0.9361. |

Magnetic rotation twice determined (64 readings) gave

| <i>t.</i> | Sp. rotation. | Mol. rotation. |
|-----------|---------------|----------------|
| 15.9°     | 1.3289        | 10.597         |

Determined once at a higher temperature (48 readings) it gave

| <i>t.</i> | Sp. rotation. | Mol. rotation. |
|-----------|---------------|----------------|
| 95.6°     | 1.1876        | 9.851          |

Diff. for 79.7° = 0.746, or for 100° = 0.936.

*Hydracetylacetone.*

Boiling point, 77° (28 mm.). Density.

|                                     |                                     |                                       |
|-------------------------------------|-------------------------------------|---------------------------------------|
| $d_{4^{\circ}/4^{\circ}}$ 1.0091.   | $d_{35^{\circ}/35^{\circ}}$ 0.9859. | $d_{70^{\circ}/70^{\circ}}$ 0.9640.   |
| $d_{5^{\circ}/5^{\circ}}$ 1.0082.   | $d_{40^{\circ}/40^{\circ}}$ 0.9825. | $d_{75^{\circ}/75^{\circ}}$ 0.9612.   |
| $d_{10^{\circ}/10^{\circ}}$ 1.0040. | $d_{45^{\circ}/45^{\circ}}$ 0.9793. | $d_{80^{\circ}/80^{\circ}}$ 0.9584.   |
| $d_{15^{\circ}/15^{\circ}}$ 1.0000. | $d_{50^{\circ}/50^{\circ}}$ 0.9761. | $d_{85^{\circ}/85^{\circ}}$ 0.9558.   |
| $d_{20^{\circ}/20^{\circ}}$ 0.9963. | $d_{55^{\circ}/55^{\circ}}$ 0.9729. | $d_{90^{\circ}/90^{\circ}}$ 0.9532.   |
| $d_{25^{\circ}/25^{\circ}}$ 0.9926. | $d_{60^{\circ}/60^{\circ}}$ 0.9699. | $d_{95^{\circ}/95^{\circ}}$ 0.9508.   |
| $d_{30^{\circ}/30^{\circ}}$ 0.9892. | $d_{65^{\circ}/65^{\circ}}$ 0.9669. | $d_{100^{\circ}/100^{\circ}}$ 0.9484. |

The magnetic rotation twice determined (56 readings) gave

| <i>t.</i> | Sp. rotation. | Mol. rotation. |
|-----------|---------------|----------------|
| 14.9°     | 1.0362        | 5.871          |

Once determined at a higher temperature (40 readings) it gave

| <i>t.</i> | Sp. rotation. | Mol. rotation. |
|-----------|---------------|----------------|
| 95.1°     | 0.9784        | 5.831          |

Diff. for 80.2° = 0.040, or for 100° = 0.050.

## 826 PERKIN: THE MAGNETIC ROTATION OF COMPOUNDS

*Ethyllic Monocarboxyethylacetoacetate.*

Boiling point, 133° (11 mm.). Density.

|                            |         |                            |         |                            |         |
|----------------------------|---------|----------------------------|---------|----------------------------|---------|
| $d\ 4^{\circ}/4^{\circ}$   | 1.1079. | $d\ 10^{\circ}/10^{\circ}$ | 1.1020. | $d\ 15^{\circ}/15^{\circ}$ | 1.0976. |
| $d\ 20^{\circ}/20^{\circ}$ | 1.0933. | $d\ 25^{\circ}/25^{\circ}$ | 1.0899. |                            |         |

The magnetic rotation twice determined (72 readings) gave—

| $t.$  | Sp. rotation. | Mol. rotation. |
|-------|---------------|----------------|
| 15.2° | 1.0172        | 10.401         |

Once determined at a higher temperature (48 readings) gave—

| $t.$  | Sp. rotation. | Mol. rotation. |
|---|---------------|----------------|
| 83.4°   | 0.9614        | 10.181         |
| Diff. for 68.26° = 0.220 or for 100° = 0.322. |               |                |

*Ethyllic  $\beta$ -ethoxycrotonate.*

Boiling point, 199—200°. Fusing point, 31°. Density.

|                            |         |                            |        |                            |         |
|----------------------------|---------|----------------------------|--------|----------------------------|---------|
| $d\ 30^{\circ}/30^{\circ}$ | 0.9788. | $d\ 35^{\circ}/35^{\circ}$ | 0.9755 | $d\ 40^{\circ}/40^{\circ}$ | 0.9723. |
|----------------------------|---------|----------------------------|--------|----------------------------|---------|

The magnetic rotation twice determined (88 readings) gave—

| $t.$ | Sp. rotation. | Mol. rotation. |
|------|---------------|----------------|
| 32.5 | 1.1611        | 10.430         |

*Methyllic Acetoacetate.*

Boiling point, 169—170° corr. Density.

|                            |         |                            |         |                            |         |
|----------------------------|---------|----------------------------|---------|----------------------------|---------|
| $d\ 4^{\circ}/4^{\circ}$   | 1.0917. | $d\ 10^{\circ}/10^{\circ}$ | 1.0855. | $d\ 15^{\circ}/15^{\circ}$ | 1.0809. |
| $d\ 20^{\circ}/20^{\circ}$ | 1.0766. | $d\ 25^{\circ}/25^{\circ}$ | 1.0724. |                            |         |

Magnetic rotation twice determined (56 readings) gave—

| $t.$  | Sp. rotation. | Mol. rotation. |
|-------|---------------|----------------|
| 15.5° | 0.9011        | 5.376          |

*Methyllic Dimethylacetoacetate.*

Boiling point 175—175.5° corr. It gave on analysis carbon 58.6 and hydrogen 8.6 per cent., the formula  $C_7H_{12}O_3$  requiring carbon 58.3 and hydrogen 8.3 per cent.

Density—

|                            |         |                            |         |                            |         |
|----------------------------|---------|----------------------------|---------|----------------------------|---------|
| $d\ 4^{\circ}/4^{\circ}$   | 1.0220. | $d\ 10^{\circ}/10^{\circ}$ | 1.0160. | $d\ 15^{\circ}/15^{\circ}$ | 1.0118. |
| $d\ 20^{\circ}/20^{\circ}$ | 1.0078. | $d\ 25^{\circ}/25^{\circ}$ | 1.0038. |                            |         |

Magnetic rotation twice determined (56 readings) gave

| $t.$   | Sp. rotation. | Mol. rotation. |
|--------|---------------|----------------|
| 15.25° | 0.9027        | 7.138          |

This substance was again treated with sodium methylate, methyllic alcohol, and methyllic iodide, it then boiled at 174—174.3°.

Density—

|                            |         |                            |         |                            |         |
|----------------------------|---------|----------------------------|---------|----------------------------|---------|
| $d\ 4^{\circ}/4^{\circ}$   | 1.0236. | $d\ 10^{\circ}/10^{\circ}$ | 1.0182. | $d\ 15^{\circ}/15^{\circ}$ | 1.0141. |
| $d\ 20^{\circ}/20^{\circ}$ | 1.0100. | $d\ 25^{\circ}/25^{\circ}$ | 1.0061. |                            |         |

Magnetic rotation once determined (64 readings) gave

|                                     |               |                |
|-------------------------------------|---------------|----------------|
| $t$ .                               | Sp. rotation. | Mol. rotation. |
| 16.5                                | 0.9026        | 7.129          |
| Average of both specimens . . . . . |               | 7.133          |

*Ethyllic Dimethylacetoacetate.*

The specimen of this substance examined boiled at  $184.8-185^{\circ}$ , and gave on combustion carbon 60.7 and hydrogen 8.92 per cent., the formula  $C_8H_{14}O_3$  requires carbon 60.76 and hydrogen 8.84 per cent.

Density—

|                            |         |                            |         |                            |         |
|----------------------------|---------|----------------------------|---------|----------------------------|---------|
| $d\ 4^{\circ}/4^{\circ}$   | 0.9915. | $d\ 10^{\circ}/10^{\circ}$ | 0.9857. | $d\ 15^{\circ}/15^{\circ}$ | 0.9813. |
| $d\ 20^{\circ}/20^{\circ}$ | 0.9773. | $d\ 25^{\circ}/25^{\circ}$ | 0.9736. |                            |         |

The magnetic rotation three times determined (96 readings) gave—

|                |               |                |
|----------------|---------------|----------------|
| $t$ .          | Sp. rotation. | Mol. rotation. |
| $17.0^{\circ}$ | 0.9117        | 8.169          |

*Ethyllic Diethylacetoacetate.*Boiling point,  $215-216^{\circ}$  corr. Density.

|                            |         |                            |         |                            |         |
|----------------------------|---------|----------------------------|---------|----------------------------|---------|
| $d\ 4^{\circ}/4^{\circ}$   | 0.9832. | $d\ 10^{\circ}/10^{\circ}$ | 0.9782. | $d\ 15^{\circ}/15^{\circ}$ | 0.9743. |
| $d\ 20^{\circ}/20^{\circ}$ | 0.9708. | $d\ 25^{\circ}/25^{\circ}$ | 0.9674. |                            |         |

Magnetic rotation three times determined (96 readings) gave—

|                |               |                |
|----------------|---------------|----------------|
| $t$ .          | Sp. rotation. | Mol. rotation. |
| $16.1^{\circ}$ | 0.9530        | 10.115         |

## REFRACTION DETERMINATIONS.

*Allylacetylacetone.*

$d\ 13.5^{\circ}/4^{\circ}$ , 0.97671.  $d\ 99.2^{\circ}/4^{\circ}$ , 0.89832.

| Line.          | $\mu$ .          |                  |                            | $\frac{\mu-1}{d}$ . |                  |                            | $\frac{\mu-1}{d}p$ . |                  |                            |
|----------------|------------------|------------------|----------------------------|---------------------|------------------|----------------------------|----------------------|------------------|----------------------------|
|                | $13.5^{\circ}$ . | $99.2^{\circ}$ . | Diff. for $85.7^{\circ}$ . | $13.5^{\circ}$ .    | $99.2^{\circ}$ . | Diff. for $85.7^{\circ}$ . | $13.5^{\circ}$ .     | $99.2^{\circ}$ . | Diff. for $85.7^{\circ}$ . |
| A .....        | 1.46156          | 1.41863          | 0.04293                    | 0.47256             | 0.46606          | 0.00650                    | 66.16                | 65.25            | 0.91                       |
| C .....        | 1.46591          | 1.42218          | 0.04373                    | 0.47703             | 0.46997          | 0.00706                    | 66.78                | 65.79            | 0.99                       |
| D .....        | 1.46986          | 1.42545          | 0.04441                    | 0.48107             | 0.47351          | 0.00746                    | 67.35                | 66.30            | 1.05                       |
| F .....        | 1.48046          | 1.43399          | 0.04647                    | 0.49192             | 0.48311          | 0.00881                    | 68.87                | 67.64            | 1.23                       |
| G .....        | 1.49009          | 1.44166          | 0.04843                    | 0.50178             | 0.49166          | 0.01012                    | 70.25                | 68.83            | 1.42                       |
| H (estim.) ... | —                | —                | —                          | —                   | —                | —                          | 71.53                | 69.94            | 1.59                       |

Dispersion  $H - A$  at  $13.5^{\circ} = 5.37$ , at  $99.2^{\circ} = 4.69$ .

*Hydracetylacetone.* $d_{8.6^{\circ}/4^{\circ}} 1.00494.$ 

| Line.        | $\mu_{8.6^{\circ}}.$ | $\frac{\mu - 1}{d}.$ | $\frac{\mu - 1}{d}p.$ |
|--------------|----------------------|----------------------|-----------------------|
| A .....      | 1.43520              | 0.43298              | 44.16                 |
| C .....      | 1.43783              | 0.43568              | 44.44                 |
| D .....      | 1.44025              | 0.43809              | 44.68                 |
| F .....      | 1.44629              | 0.44409              | 45.30                 |
| G .....      | 1.45130              | 0.44908              | 45.81                 |
| H (estim.).. | —                    | —                    | 46.18                 |

The dispersion equivalent from the above for H—A is 2.02, calculated 1.98.

*Ethyl ethoxycrotonate.* $d_{32.4^{\circ}/4^{\circ}} 0.97245.$ 

| Line.        | $\mu_{32.4^{\circ}}.$ | $\frac{\mu - 1}{d}.$ | $\frac{\mu - 1}{d}p.$ |
|--------------|-----------------------|----------------------|-----------------------|
| A .....      | 1.43965               | 0.45210              | 71.43                 |
| C .....      | 1.44327               | 0.45583              | 72.02                 |
| D .....      | 1.44709               | 0.45976              | 72.64                 |
| F .....      | 1.45589               | 0.46881              | 74.07                 |
| G .....      | 1.46364               | 0.47677              | 75.33                 |
| H (estim.).. | —                     | —                    | 76.40                 |

The dispersion equivalent from the above for H—A is 4.97, calculated 3.13.

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