

XCVIII. — *Absorption Spectra and Tautomerism.*  
*Part II. Ethyl Mesityloxidoxalate, Formylphenyl-*  
*acetate, and Diacetylsuccinate.*

By RICHARD ALAN MORTON and EDWARD ROGERS.

*Ethyl Mesityloxidoxalate.*

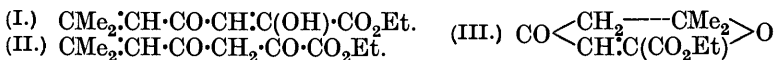
THREE modifications of ethyl mesityloxidoxalate have been isolated: (i)  $\alpha$ , m. p.  $21^{\circ}$ ; (ii)  $\beta$ , m. p.  $59-60^{\circ}$ ; (iii) a dimeric form, m. p.  $175^{\circ}$  (Federlin, *Annalen*, 1907, **356**, 261). These can be converted into one another as follows:

$\beta \rightleftharpoons \alpha$  in the dark, equilibrium being reached after about 12 weeks.

$\alpha \rightarrow \beta \rightarrow$  dimeride in diffuse daylight, with precipitation of the dimeride from most solvents.

The  $\alpha$ -form develops a red colour with ferric chloride and is undoubtedly the enolic form (I). Claisen at first regarded the

$\beta$ -form as a dihydropyrone derivative (III) (*Ber.*, 1891, **24**, 116), but later he formulated it as the ketone (II).



Dieckmann (*Ber.*, 1920, **53**, 1772) regards the  $\alpha$ -form as enolic, but rejects the ketonic formula for the  $\beta$ -form, on the ground that the small percentage of enol in the equilibrium mixture is not in accordance with Claisen's rule that the velocity of enolisation and the enol content of the equilibrium mixture increase with increasing acidity of the acyl groups: moreover, the  $\alpha$ -ester when distilled passes mainly into the  $\beta$ -ester. Dieckmann and von Auwers (*Ber.*, 1923, **56**, 1527) regard the refractometric data for the fused material as confirming the structure (III), and Borsche and Thiele (*Ber.*, 1923, **56**, 2132) find further confirmation in the fact that the catalytic hydrogenation of the  $\alpha$ -ester is more rapid than that of the  $\beta$ -ester.

This example of tautomerism is interesting in several respects.

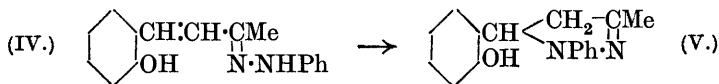
(1) The equilibrium can be studied either as a reversible or as an irreversible one.

(2) The  $\beta$ -form can be examined under conditions such that the enolic tautomeride is excluded.

(3) The relatively slow rate of change renders the course of the reactions amenable to spectrographic investigation.

In the preceding paper definite conclusions have been drawn concerning the absorption spectra of keto-enol tautomerides. The results of an examination of ring-chain tautomerides are now recorded. We are greatly indebted to Dr. A. McGookin of this University, who suggested and synthesised the compounds of this nature.

Spectrographic evidence shows that keto-enol tautomerides exhibit absorption maxima at the same wave-length but with differing absorptive power. In the cases of pure ring-chain tautomerism without elimination of water, *e.g.*,



(IV) shows two bands at 3600 Å. and 2545 Å. and (V) shows one band at 2790 Å. Ring-chain tautomerides thus differ markedly from keto-enol tautomerides in absorption spectra.

The dimeric modification of ethyl mesityloxidoxalate shows no selective absorption and the continuous absorption is relatively feeble, so that the presence of this form does not seriously interfere with the absorption of the  $\beta$ -form in various solvents.

The  $\beta$ -form in alcohol, hexane, or chloroform shows a well-defined band of high extinction coefficient, with  $\lambda$  (max.) varying a little for the different solvents. The enolic modification shows another band of high extinction coefficient, and a less noticeable shift due to the solvent. When a solution of the  $\alpha$ -form in any of the three solvents used was kept, the position of maximum absorption shifted towards the ultra-violet and the measured absorption curve was the sum of the curves due to the  $\alpha$ - and  $\beta$ -forms.

The  $\beta$ -form in presence of alkali shows three bands at  $\lambda$  (max.) 3512, 2867, and 2450—2500 Å. The first and the third are developed when alkali is added to the  $\alpha$ -(enolic) modification and are also shown by the pure sodium derivative. If alkali is added to the  $\beta$ -form, the system will contain unchanged  $\beta$ -ester and the sodium salt of the  $\alpha$ -ester. Hence the observed curve is a summation of two curves, one with a maximum at 2825 Å. due to the  $\beta$ -ester and the other with maxima at 3510 and 2457 Å., due to the sodium derivative of the  $\alpha$ -ester.

An alcoholic solution of the  $\beta$ -compound to which a large excess of sodium ethoxide had been added was left on ice. Later it was saturated with dry hydrogen chloride, and the sodium chloride filtered off. The solution then showed only one band, namely, the 3120 band due to the enolic ester.

The spectrographic data show that the reversible  $\alpha \rightleftharpoons \beta$  isomerism of ethyl mesityloxidoxalate resembles ring-chain tautomerism rather than keto-enol tautomerism. This conclusion is in agreement with the most recent chemical evidence. The metallic derivatives are probably co-ordinated compounds.

### Summary of Results.

| Substance.                           | $\lambda$ (max.). | $e$ (max.). | $\lambda$ (min.). | $e$ (min.). |      |        |      |      |
|--------------------------------------|-------------------|-------------|-------------------|-------------|------|--------|------|------|
| Ethyl $\beta$ -mesityloxidoxalate :  |                   |             |                   |             |      |        |      |      |
| Fresh solution in alcohol ...        | 2825              | 12,200      | 2275              | 3800        |      |        |      |      |
| "  "  "  hexane ...                  | 2775              | 11,500      | 2310              | 3300        |      |        |      |      |
| "  "  "  chloroform                  | 2850              | 11,500      | 2460              | 3700        |      |        |      |      |
| Alcoholic solution plus 10           | {                 | }           | }                 | }           |      |        |      |      |
| equivs. of NaOEt .....               |                   |             |                   |             | 3512 | 13,000 | 3010 | 3700 |
|                                      |                   |             |                   |             | 2867 | 7,500  | 2320 | 3400 |
|                                      | 2495              | 7,500       | —                 | —           |      |        |      |      |
| Ethyl $\alpha$ -mesityloxidoxalate : |                   |             |                   |             |      |        |      |      |
| Fresh solution in alcohol ...        | 3125              | 14,200      | 2415              | 3950        |      |        |      |      |
| "  "  "  hexane ...                  | 3122              | 14,000      | 2420              | 3900        |      |        |      |      |
| "  "  "  chloroform                  | 3125              | 15,100      | 2475              | 4750        |      |        |      |      |
| Alcoholic solution plus 1            | {                 | }           | }                 | }           |      |        |      |      |
| equiv. of NaOEt .....                |                   |             |                   |             | 3510 | 16,500 | 2825 | 3500 |
|                                      |                   |             |                   |             | 2457 | 6,750  | —    | —    |
| 10 equivs.  "  .....                 | {                 | }           | }                 | }           |      |        |      |      |
|                                      |                   |             |                   |             | 3510 | 18,700 | 2825 | 3750 |
|                                      | 2457              | 9,200       | —                 | —           |      |        |      |      |
| 100 equivs.  "  .....                | {                 | }           | }                 | }           |      |        |      |      |
|                                      |                   |             |                   |             | 3510 | 21,250 | 2870 | 3800 |
|                                      | 2457              | 9,200       | —                 | —           |      |        |      |      |

*Ethyl Formylphenylacetate.*

Four forms of this substance have been recorded :

- (1) Liquid, b. p. 135°/15 mm. ; enolic.
- (2) Solid, m. p. 70° ; regarded as an aldo-form or as a geometrical isomeride of (3).
- (3) Solid, m. p. 100—110°.
- (4) Solid, m. p. 50° (Michael's modification .

Doubtless these forms are not all isomerides. Wolf (*J. Physical Chem.*, 1900, **4**, 123) has shown that by keeping the ester at different temperatures for long periods it can be made to melt at any temperature between 50° and 100°, the former temperature being a stable triple point in the phase diagram. The difference in m. p. and refractivity of the various forms is due to one or more of the alternatives : (1) keto-enol tautomerism, (2) stereoisomerism, (3) unequal degrees of association. Michael and Fuller (*Annalen*, 1912, **391**, 275) have adduced evidence that all the forms are unimolecular. The conclusion is drawn that only three forms exist having b. p. 125°/9 mm., m. p. 40°, and m. p. 100—103°, respectively, all of which are enolic, since they react with aliphatic tertiary amines.

Wislicenus, however, after studying the isomerism of ethyl formylphenylacetate over a period of 30 years, draws the conclusion that the only two forms possessing real existence are ( $\alpha$ ), b. p. 125—126°/9 mm., and ( $\beta$ ), m. p. 103—105°. All other "forms" he regards as mixtures of the  $\alpha$ - and the  $\beta$ -form. These he considers, after reviewing all the available evidence, to be *cis*- and *trans*-isomerides.

Together with his pupils he has studied the methyl formylphenylacetates and has found two modifications : ( $\alpha$ ), m. p. 40—41°, and ( $\beta$ ), m. p. 91—93°. No mixtures occur.

The  $\alpha$ -modification is undoubtedly enolic, but the  $\beta$ -form presents difficulties, since it is doubtful whether it exists as an aldo-form or as a geometrical isomeride of the  $\alpha$ -form. The two modifications react differently with copper acetate, and the  $\beta$ -form will under no conditions develop a coloration with ferric chloride. The anilides and piperidides of formylphenylacetic acid give two modifications, both of which are enolic. Michael considers that the aldo-modification has never been isolated and that much of the earlier work was misinterpreted owing to the fact that the  $\beta$ -form can add on a molecule of alcohol. For example, methyl formylphenylacetate-

methyl alcoholate is a crystalline substance, m. p. 89—92°, which does not develop a colour with ferric chloride.

Dieckmann (*Ber.*, 1917, **50**, 1375) concludes that the ethyl ester exists in the pure state only as a liquid enol,  $\alpha$ , and a solid, m. p. 110°, which also is enolic.

Preparations of ethyl formylphenylacetate were examined having b. p. 127°/10 mm., m. p. 70°, and m. p. 100°, respectively. No maxima were found in the absorption curves, which were similar in extinction coefficient (order 7500 at 2600 Å.) and inflexions (2600—2100). With alkali, a definite band was obtained with a maximum at 2740 ( $e$  max. 19,200, 22,200, 16,800).

The interpretation of these results is somewhat difficult. Although ketones show well-defined maxima, in this substance the carbonyl group is a part of the formyl radical, so that the absence of the ketonic band does not prove the non-existence of an aldo-form. The data do not show the very large variations of  $e$  which are observed in keto-enol tautomerism. The absorptive powers of *cis*- and *trans*-isomerides (Errara and Henri, *Compt. rend.*, 1925, **181**, 549) for a given wave-length are in the ratio 1 : 1—2, generally near 1.0—1.2. This is precisely the kind of variation observed in ethyl formylphenylacetate. Hence the spectrographic data strongly support the conclusion that the isomerism of this substance is of the *cis*- and *trans*-variety.

#### *Ethyl Diacetylsuccinate.*

The isomerism of this ester has been the subject of much controversy. Two definite modifications were isolated and examined spectrographically :

Isomeride, m.p. 92°;  $\lambda$  (max.) = 2490,  $e$  (max.) 7600.

Isomeride, m. p. 31°;  $\lambda$  (max.) = 2490,  $e$  (max.) 6250.

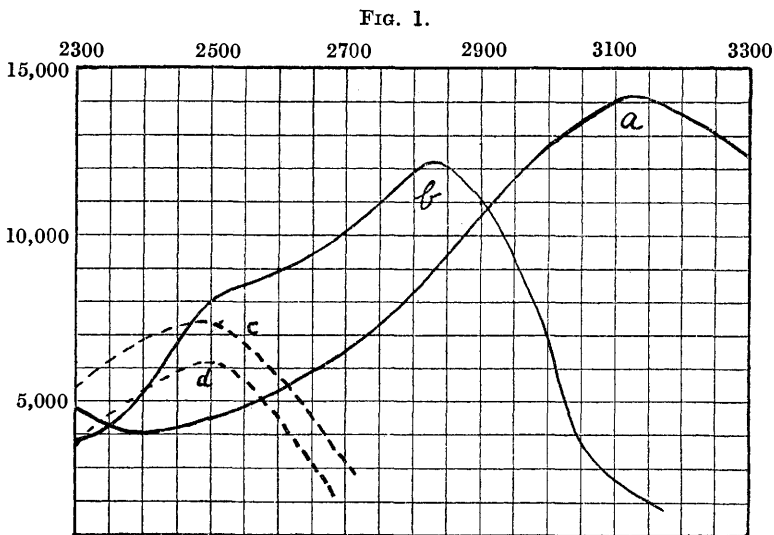
With alkali both forms exhibit a band at  $\lambda = 2750$  ( $e$  max. varying with the alkali/ester ratio).

The two substances provide an interesting comparison with ethyl acetoacetate :

|                            | Acetoacetate.               | Diacetylsuccinate.         |
|----------------------------|-----------------------------|----------------------------|
| Enol band .....            | 2430Å.; $e$ , 10,000        | 2490Å.; $e$ , 7600<br>6250 |
| Keto band .....            | 2700Å. app.; $e$ order 100. | unknown.                   |
| Co-ordinated sodium salt   | $\lambda$ (max.) 2725.      | $\lambda$ (max.) 2750.     |
| Ratio of extinctions ..... | enol/keto = 100 : 1 (order) | m.p. 92°/m.p. 31° = 1.22.  |

The following results are from Henri and Errara's work. The

figures denote the ratio of  $e$  for the *trans*-isomeride to  $e$  for the *cis*-isomeride at the wave-lengths cited.



(a) Ethyl  $\alpha$ -mesityloxidoxalate in alcohol. (b) Ethyl  $\beta$ -mesityloxidoxalate in alcohol. (c) Ethyl diacetylsuccinate, *m. p.* 92°, in alcohol. (d) Ethyl diacetylsuccinate, *m. p.* 31°, in alcohol.

| Substances. | $\lambda$ 2520Å. | $\lambda$ 2410Å. |
|-------------|------------------|------------------|
| CHCl:CHCl   | 1.4              | 2                |
| CHEt:CHBr   | 1.15             | 1.2              |
| CHMe:CHBr   | 1.5              | 1.5              |
| CHI:CHCl    | 1.3              | 1.25             |

Hence the data provide strong support for the view that the isomerism of ethyl diacetylsuccinate is of the *cis-trans* type.

One of us (E. R.) wishes to express his gratitude to the Advisory Council of the Department of Scientific and Industrial Research for a maintenance grant. We are very grateful to Professor E. C. C. Baly, C.B.E., F.R.S., whose advice and encouragement have been of great value to us.

THE UNIVERSITY, LIVERPOOL.

[Received, December 16th, 1925.]