XXI.—*The Relation between Absorption Spectra and Chemical Constitution. Part XIII. Some Pyrones and Allied Compounds.*

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THE question of the constitution of the pyrones and their derivatives has been discussed at considerable length by Feist, Claisen, and Collie, but only from a chemical standpoint. The subject is a difficult one, being complicated by the possible presence of quadrivalent oxygen, but for this reason presents a greater interest. The only physical measurements made up to the present are those of the molecular refractions by Miss Homfray (*Trans.*, 1905, **87**, 1443) in a paper which is a very valuable contribution to the literature dealing with these compounds. In every compound examined, Miss Homfray obtained values for the molecular refractivity which were considerably higher than the additive values calculated from the usually accepted molecular formulæ. This excess value was attributed by the author to the presence of quadrivalent oxygen, and formulæ were given to the compounds examined involving the presence of one or more atoms of quadrivalent oxygen. For example, the formula of dimethylpyrone put forward by Collie (*Trans.*, 1904, **85**, 973),

was adopted—a formula which satisfies in a very marked way the abnormal properties of this compound, as for example, its inability to form an oxime or phenylhydrazone. The hydrochloride of dimethylpyrone would then be represented by the formula

which agrees extremely well with the molecular refractivity, involving,

as it does, two quadrivalent oxygen atoms. Using the above formula for dimethylpyrone, the atomic refractivity of quadrivalent oxygen was found by Miss Homfray to be 2.65, and the value obtained from the above formula of the hydrochloride was 2.79. These two values are in very good agreement, and, moreover, the increase in refractivity incurred in passing from the base to its salt is of very considerable importance, as will be shown below. Since the appearance of Miss Homfray's paper, a considerable amount of work has been carried out by Brühl (Trans., 1907, 91, 115) and others, dealing with the influence of contiguous double linkings on molecular refractivity, the presence of these contiguous double linkings always giving an exalted value for the refractivity, that is to say, a value which is greater than the purely additive value as obtained from the simple graphic formula of the compound. It would appear that some of the refractivities obtained by Miss Homfray for the other compounds examined by her are subject to a correction for this reason. It is impossible to estimate the magnitude of this correction in the light of our present knowledge, but it is not improbable that the exalted values of refractivity in many cases are partly due to this cause and are not entirely to be attributed to the presence of quadrivalent oxygen.

It was thought that independent evidence of the constitution of dimethylpyrone and the allied compounds might be obtained from an examination of their absorption spectra, and consequently we have examined all the available compounds of this type; the present paper contains an account of the results obtained in the more important cases.

The first compounds examined were 4-pyrone, 2:6-dimethyl-4-pyrone, and 2:3:5:6-tetramethyl-4-pyrone, and it was found that the absorption curves of the three are essentially the same. The absorption of the first two compounds in alcoholic solution is shown in Fig. 1, curves 1 and 4, the curve of tetramethylpyrone being so similar to that of dimethylpyrone as not to justify its reproduction. It is evident that not one of these compounds shows an absorption band, there being only a somewhat rapid extension of the curves at higher concentrations. The addition of hydrogen chloride to the alcoholic solution causes this extension to disappear, as can be seen from curve 5, Fig. 1, which shows the absorption of dimethylpyrone in presence of considerable excess (50 equivalents) of hydrochloric acid. The small amount of absorption exhibited by these curves cannot in any way be reconciled with the ordinary pyrone formula, namely,

for not only is there a carbonyl group situated between two ethylenic
VOL. XCV. L

double linkings, but there is also the added effect of the unsaturated oxygen atom in the ring. On the other hand, the bridged-ring structure put forward by Collie (*loc. cit.*) would naturally give rise to the small amount of general absorption we have observed. The slight extension on the absorption curve would then arise from the play of forces between the residual affinity of the central or bridged oxygen and the three double linkings of the ring. This view is

FIG. 1.

Oscillation frequencies.

1. 4-Pyrone in alcohol.
2. " + 1 equivalent of NaOEt.
3. " + 60 equivalents of NaOEt.
4. Dimethylpyrone in alcohol.
5. " + great excess of HCl.
6. " + 87 equivalents of NaOEt.
7. " in water + 100 equivalents of NaOH.

supported by the fact that in the presence of hydrogen chloride this sudden extension on the absorption curve is entirely eliminated.

A very significant fact referred to above is that the molecular refractivity of the hydrochloride of dimethylpyrone has an even greater exalted value than the free base. If, as might possibly be

suggested, the exalted values given by the free base were due to some arrangement of contiguous double linkings, it would be impossible to conceive how this could be further exalted by the removal of some of the residual affinity consequent on the addition of one molecule of hydrogen chloride.

The evidence, therefore, is very strongly in favour of the bridged-ring formula for the pyrones, since this formula satisfies the values obtained with the refractometer and the spectroscope, and also is supported by their chemical behaviour.

A very marked change in the absorption of the pyrones is manifested on the addition of sodium ethoxide to their solutions in alcohol. Curves 2 and 3, Fig. 1, show the absorption of pyrone in presence of one and sixty equivalents of sodium ethoxide respectively. A well-marked absorption band is now produced with the one equivalent and intensified with the sixty equivalents. Very similar results are produced with dimethylpyrone, only in this case a greater relative concentration of sodium ethoxide is required (Fig. 1, curve 6). The curve in the latter case is very strikingly similar to that given by γ -lutidone in presence of hydrogen chloride (Baker and Baly, *Trans.*, 1907, **91**, 1122), and, moreover, the chemical evidence shows that an additive compound of dimethylpyrone and sodium ethoxide is formed (Collie and Steele, *Trans.*, 1900, **77**, 970). The analogy to lutidone hydrochloride suggests at once that the additive compound is to be represented by

$$\begin{array}{c} \text{Na} \\ \text{EtO} \end{array} > \text{O} < \begin{array}{c} \text{CMe} \cdot \text{CH} \\ \text{CMe} \cdot \text{CH} \end{array} > \text{CO}.$$

As was pointed out in the previous paper, lutidone hydrochloride is very similar in its absorption to phorone, where a carbonyl group is situated between two double linkings, so that the spectroscopic evidence is in favour of the addition of the sodium ethoxide to dimethylpyrone as in the above formula. There is thus a very striking difference in the addition of hydrogen chloride and of sodium ethoxide to dimethylpyrone, for the former unites with the oxygen atom in the bridge, whilst in the latter case, the addition takes place to the oxygen atom in the ring, the bridge being first ruptured.

The effect of the addition of alkali to an aqueous solution of dimethylpyrone is entirely different from that obtained in alcoholic solution, as can be seen from curve 7, Fig. 1. It is well known that the addition of alkali to an aqueous solution of dimethylpyrone tends to give the sodium salt of diacetylacetone, and, indeed, the absorption curve obtained approximates to that of diacetylacetone in aqueous alkali (Fig. 2, lower curve 2), so that no doubt a considerable quantity of this substance is formed.

The results obtained from the spectroscopic examination of diacetylacetone have proved somewhat complex, owing to the various forms in

which this substance might exist. It is evident from its empirical formula that it might exist either as a hydrate of dimethylpyrone or as an open-chain compound. There are thus three different possibilities as follows :

FIG. 2.
Oscillation frequencies.

- Upper curves—1. Dimethylpyrone: ethyl alcohol compound.
 2. " " " " + 2 equivalents of NaOEt.
 3. Pyromeconic acid.
 4. " " " " + 4 equivalents of NaOEt.
- Lower curves—1. Diacetylacetone in water.
 2. " " " " + 10 equivalents of NaOH.
 3. " " " " in alcohol.
 4. " " " " + 9 " " NaOEt.

and, further, of these, (III) might exist in one of the possible enolic forms.

Now the absorption curves of diacetylacetone in aqueous and alcoholic solutions (Fig. 2, lower curves 1 and 3) are entirely different from one another, but whatever may be the final interpretation, there is no doubt that formula (I) above must be ruled out of court, for neither of the two curves bears the slightest resemblance to that of dimethylpyrone hydrochloride. We are therefore left with the two forms (II) and (III), and in order to test the validity of (III), or rather the dynamic equilibrium of the ketonic and enolic forms, we have examined the absorption spectrum of tetra-acetylene, which possesses an analogous structure to (III). The absorption of the latter compound is shown on Fig. 3, lower curves 3 and 4, in neutral and alkaline solutions respectively. The type of absorption closely resembles that of diacetylacetone in aqueous solution, and, indeed, the absorption of both these compounds is of the keto-enolic type, as exemplified by acetylacetone, etc. (Baly and Desch, *Trans.*, 1904, 85, 1029). There is therefore every justification for the conclusion that diacetylacetone in aqueous solution exists in the open-chain configuration, and that it is a dynamic equilibrium mixture of the ketonic and enolic forms.

The case is different when the compound is dissolved in alcohol, for the absorption curve shows a most exceptionally broad band. It is, however, of some importance to note that this band covers the region occupied by the band given by an alcoholic solution of dimethylpyrone in presence of sodium ethoxide and the band of diacetylacetone in aqueous solution. Now it is clear that if the diacetylacetone had the form (II), its absorption would conform more or less to that of pyrone in presence of alcoholic sodium ethoxide; the absorption, however, is compounded of that of the open-chain formula and of that of pyrone in alcoholic sodium ethoxide. For this reason it appears certain that diacetylacetone in alcoholic solution exists in *both* forms, (II) and (III). This conclusion is borne out by the fact that under certain conditions the alcoholic solution shows the broad absorption band subdivided into two, one due to form (II) and the other due to form (III). The addition of sodium ethoxide to the alcoholic solution of dimethylpyrone still further supports this conclusion, for two absorption bands are exhibited (Fig. 2, lower curve 4), one almost the same as that of dimethylpyrone in presence of alcoholic sodium ethoxide (Fig. 1, curve 6), and the other the same as diacetylacetone in presence of aqueous alkali (Fig. 2, lower curve 2).

In Fig. 2, upper curves 1 and 2, is shown the absorption of the alcohol compound of dimethylpyrone in neutral and alkaline alcoholic solution respectively. A comparison of the latter with Fig. 1,

curve 6, shows at once that at the strength employed ($N/100$), 87 equivalents of sodium ethoxide only partly convert the dimethylpyrone into the additive compound. From analogy to diacetylacetone, the formula of the alcohol compound of dimethylpyrone would appear to be

and is therefore the monomethyl ether of diacetylacetone. It is interesting to compare the readiness with which this compound loses alcohol and diacetylacetone loses water. Whereas, in the former case, the molecule of alcohol is removed with the greatest of ease, diacetylacetone only loses its water with difficulty. This may be represented in another way by comparing the two reversible processes:

In (a) there is no tendency for the open-chain compound to be formed, but the intermediary compound prefers to pass into the pyrone; in (b), on the other hand, the open-chain compound is the most favoured in aqueous solution, and in alcoholic solution there is present some of the intermediary compound, probably in equilibrium with the open-chain form. The tendency is for the intermediary compound to pass into the open-chain; therefore it will only lose water with difficulty to give the pyrone.

Two derivatives of pyrone may next be dealt with, namely, pyromeconic acid and triacetic lactone, the absorption spectra of which are shown on the upper portions of Figs. 2 and 3. Pyromeconic acid (2-hydroxy-4-pyrone) in neutral alcoholic solution (Fig. 2, upper curve 3) is very interesting, for it exhibits a shallow absorption band which must arise from the influence of the hydroxyl group. An almost identical curve is given by triacetic lactone ethyl ether (Fig. 3, upper curve 3), showing that these two compounds possess an analogous structure. The head of the absorption band in each case is at about $1/\lambda = 3000$, and therefore it is not possible that the conjugate linking occurs; in other words, their structure cannot be represented by the two formulæ:

Pyromeconic acid.

Triacetic lactone ethyl ether.

Doubtless the bridged ring is also present in each case, and therefore the absorption band is due to the influence of the hydroxylic oxygen in each case. The addition of sodium ethoxide to the solution of pyromeconic acid produces an effect quite analogous to that

FIG. 3.

Oscillation frequencies.

Upper curves—1. *Triacetic lactone.*

2. " " +5 equivalents of NaOEt.

3. " " *Ethyl ether.*Lower curves—1. *Ethyl ester of triacetic acid.*

2. " " +5 equivalents of NaOEt.

3. *Tetra-acetylene.*

4. " +10 equivalents of NaOEt.

observed with 4-pyrone itself. A similar additive compound is formed with the rupture of the bridge, with the result that the absorption curve obtained (Fig. 2, upper curve 4) is almost identical with that of the additive compound of pyrone and sodium ethoxide (Fig. 1, curve

2). The absorption band is now produced by the contiguous double linkings, as expressed in the formula :

Triacetic lactone, on the other hand, has not the same structure as its ethyl ether, for a much deeper absorption band is produced (Fig. 3, upper curve 1). This difference, however, is in all probability to be explained by the lactone existing in the ketonic form,

the absorption band being due to the presence of some enol-ketonic tautomerism as in the case of camphor, to which, indeed, the absorption spectrum closely approximates.

The addition of a small quantity of sodium ethoxide to the alcoholic solution of triacetic lactone is only sufficient to form the sodium salt, with no essential alteration in the absorption spectrum. As in the case of dimethylpyrone, a small quantity of sodium ethoxide is not sufficient to break the bridge with the formation of the additive compound. The presence of the methyl group restrains the formation of the additive compound in both cases. The discussion of this point may be reserved until later.

The absorption curves of ethyl triacetate are shown in Fig. 3, lower curves 1 and 2 ; this open-chain compound,

exhibits an absorption similar to that of tetra-acetyethane and of the open-chain form of diacetylacetone.

A very striking proof of the existence of the bridged-ring structure of the pyrones is to be found in the case of diacetyldimethylpyrone, the absorption curve of which is shown in Fig. 4, curve 5. There is only slight general absorption, which is entirely incompatible with the ordinary formula :

which possesses no fewer than five contiguous double linkings. If these linkings had free play, the compound would undoubtedly be coloured yellow and exhibit very strong absorption. The bridged-ring

form is, however, free from this objection, as may readily be seen :

or the structure is comparable with a benzenoid compound, where, as is well known, the benzenoid dynamic activity is restrained by the substitution by acetyl and other electronegative groups. In this case, as in the other pyrones, the ring is ruptured on the addition of sodium

FIG. 4.
Oscillation frequencies.

1. *Dehydracetic acid.*
2. „ „ „ + 10 equivalents of NaOEt.
3. *Dimethylpyronecarboxylic acid.*
4. *iso Dehydracetic acid.*
5. *Diacetyldimethylpyrone.*
6. „ „ „ + 2 equivalents of NaOEt.

ethoxide, a yellow compound being formed, the absorption of which is shown in Fig. 4, curve 6. As is evident from the formula :

the double linkings have now free play, with the formation of an absorption band as high up the spectrum as $1/\lambda = 2180$.

Quite similar arguments are applicable to chelidonic acid and its ethyl ester, for the absorption of these compounds in alcoholic

solution (curve 1, Fig. 5) is quite impossible if the structure were represented by

and, as in the case of diacetyldimethylpyrone, the bridged-ring structure must be present in order to account for there being only small general absorption. The formula may therefore be written

FIG. 5.
Oscillation frequencies.

1. Chelidonic ethyl ester.
2. " " in dry alcohol + 100 equivalents of NaOEt.
3. " " acid + 100 equivalents of NaOH in water.
4. Xanthochelidonic ethyl ester in anhydrous chloroform.
5. " " in water.
6. " " in alcohol.
7. " " + 100 equivalents of NaOEt.

The addition of sodium ethoxide to the alcoholic solution, or of sodium hydroxide to the aqueous solution, as in the previous cases, forms a yellow additive compound with the consequent rupture of the bridge, so that there is every possibility for the free play of forces between the five contiguous double linkings (Fig. 5, curves 2 and 3).

Ethyl xanthochelidonate, the empirical formula of which corresponds with an additive compound of ethyl chelidonate and water, naturally exhibits very considerable absorption, since the bridged

structure is no longer possible, and generally speaking the five contiguous linkings have free play. There is, however, very considerable difference in the absorption of this compound according to the nature of the solvent. In perfectly dry chloroform or ether, the substance forms a colourless solution, and the absorption exhibited is shown in Fig. 5, curve 4, there being present one absorption band with its head at about $1/\lambda = 3000$. The addition of the slightest trace of water causes the solution to become intensely yellow, and since the amount of water is far less than is necessary to form an additive compound, this must be due to an isomeric change. On the other hand, the solution in alcohol in the presence of sodium ethoxide shows two absorption bands, one at $1/\lambda = 2450$ and the other at $1/\lambda = 3500$. This latter spectrum is quite analogous to that of ethyl chelidonate as obtained in aqueous alkaline solution, and would appear to be due to the sodium compound of the ester,

For this reason we are inclined to the view that ethyl xanthochelidonate in anhydrous chloroform or ether exists in the open-chain form, $\text{CO}_2\text{Et}\cdot\text{C}(\text{OH})\text{:CH}\cdot\text{CO}\cdot\text{CH}\cdot\text{C}(\text{OH})\cdot\text{CO}_2\text{Et}$, an explanation which might also account for the abnormally high values of the refractivity found by Miss Homfray for this compound in the former solvent. On these grounds the absorption results obtained with solutions in alcohol and in water (Fig. 5, curves 6 and 5) would be due to mixtures of the two forms, the closed ring,

and the open chain.

A comparison of ethyl chelidonate and ethyl xanthochelidonate and their absorption spectra may be made, for the formulæ of the additive compounds may be written as follows:

Ethyl chelidonate in alcohol
with sodium ethoxide.

(I.)

Ethyl xanthochelidonate in alcohol
with sodium ethoxide.

(II.)

The two compounds differ merely by the replacement of the ethyl group in (I) by sodium in (II). That these compounds would differ in their absorption follows from a comparison of the esters and sodium salts of the unsaturated aromatic acids (Baly and Schaefer, *Trans.*, 1908, **93**, 1808), and their spectra are shown in Fig. 5, curves 2 and 7 respectively. The addition of sodium hydroxide to a solution of chelidonic acid would tend to give substance (II) above; this is in agreement with the absorption obtained, as shown in Fig. 5, curve 3,

which is very similar to curve 7, the slight difference being due no doubt to the fact that the acid was used in place of the ester.

We have also examined the absorption spectrum of dehydracetic acid, isodehydracetic acid, and dimethylpyronecarboxylic acid. The curves for the first-named substance are shown in Fig. 4 (curves 1 and 2), and it may be seen at once that the addition of sodium ethoxide shifts the band towards the shorter wave-lengths, which is quite exceptional in these compounds. Two formulæ have been proposed for dehydracetic acid, one by Feist and the other by Collie :

Whichever be the correct formula, it is evident that the ring must be bridged, for otherwise, the addition of alkali would increase the absorption considerably. Consequently the question of constitution lies between the two forms :

The very close similarity between triacetic lactone and dehydracetic acid in presence of alkali is necessarily strongly in favour of (I), since in (II) there is one more carbonyl group in direct conjugation than in triacetic lactone, which would presumably increase the play of forces and so alter the absorption. The increase of absorption in the free compound does not seem to follow, however, from either of the formulæ.

The absorption spectrum of dimethylpyronecarboxylic acid is shown in Fig. 4, curve 3, and presents some considerable interest. The formula of this compound from the method of preparation depends on that of dehydracetic acid. Two are possible, namely :

and, of these, (I) would follow if Collie's formula for dehydracetic acid were correct, and (II) if that of Feist were true. We have observed that the addition of sodium ethoxide to the alcoholic solution of this acid does not at once produce any very marked change in the absorption, but if this solution is kept standing for about a week, the type of absorption is quite altered and becomes like that of the open-chain form of diacetylacetone. It appears, therefore, that this acid, even in alcoholic solution in the presence of sodium ethoxide, is inclined to open up and favour the open-chain form. This tendency will

naturally be antagonistic to the formation of the bridged ring, which is the final condensed form of the pyrones. Consequently in this compound we should expect to find some evidence that the whole does not exist in the bridged-ring form, and, indeed, the absorption curve shows a sudden extension or incipient absorption band in the same region of the spectrum as the band of the addition compound of dimethylpyrone and sodium ethoxide. Dimethylpyronecarboxylic acid, therefore, must exist in alcoholic solution to a great extent as

Since the region of the absorption is the same as that of the compound of dimethylpyrone and sodium ethoxide, formula (I) is the more probable, since (II) introduces a further conjugation of the carbonyl portion of the carboxyl group. This would mean, therefore, that Collie's formula is the more probable for dehydracetic acid, which agrees with the conclusion drawn above for this substance.

It is possible that the reason for this abnormal behaviour of dimethylpyronecarboxylic acid lies in the CH_2 group of the side-chain. It has been previously shown that in compounds of the type of benzyl methyl ether and benzyl alcohol, which contain in the side-chain a CH_2 group and some group possessing residual affinity, the absorption and dynamic activity of the benzene nucleus are much modified (Baly and Collie, *Trans.*, 1905, **87**, 1332). The influence of a CH_2 group in this way is often very pronounced, although the reason for this is obscure (Baly and Tuck, *Trans.*, 1908, **93**, 1902), and, further, it is not improbable that the increased absorption of dehydracetic acid (which is doubtless ketonic) in neutral solution is due to this cause.

Finally, we have observed the absorption spectrum of *isodehydracetic acid*, which is shown in Fig. 4, curve 4, although the substance does not belong to the class of 4-pyrones.

A reference was made above to the much greater readiness with which sodium ethoxide forms the additive compound with pyrone than it does with dimethylpyrone. This fact was also noticed in the case of pyromeconic acid and triacetic lactone, for the addition takes place much more readily in the former case. In the case of pyrone one equivalent of sodium ethoxide is sufficient to form a considerable quantity of the additive compound, whereas upwards of eighty equivalents are required in the case of dimethylpyrone. Again, four equivalents are sufficient in the case of pyromeconic acid, and ten equivalents are entirely insufficient with triacetic lactone. There is therefore no doubt that the presence of the methyl groups on the neighbouring carbon atoms materially decreases the activity of the

oxygen atom, this being comparable with the effect already examined in the ketones (Stewart and Baly, *Trans.*, 1906, **89**, 507). This fact brings the observations within the class of phenomena usually known as steric hindrance.

Conclusions.

1. The results obtained indicate that pyrone, dimethylpyrone, and tetramethylpyrone exist in solution in the bridged-ring form.

2. Diacetylacetone in aqueous solution exists in the open-chain form and is an equilibrium mixture of the enolic and ketonic forms. In alcoholic solution this compound exists partly in the closed-ring form, that is to say, as a hydrate of dimethylpyrone.

3. Pyromeconic acid, triacetic lactone, diacetyldimethylpyrone, chelidonic acid, and its ethyl ester all possess the bridged-ring structure.

4. The bridge structure thus typical of the pyrones is broken in the presence of sodium ethoxide, due to the formation of an additive compound in each case, the addition of the sodium ethoxide being to the atom of oxygen in the ring.

5. Ethyl xanthochelidonate appears to exist in the open-chain form in dry ether or chloroform solution, which solutions are both colourless. In alcoholic or aqueous solution it exists as a mixture of the open-chain and closed-ring forms, and in alcoholic solution in presence of sodium ethoxide, entirely as the sodium salt of the closed-ring form.

6. The absorption spectrum of dehydracetic acid indicates that Collie's formula is more probable for this compound than that of Feist. This would lead to the conclusion that the so-called dimethylpyrone- β -carboxylic acid has not this formula, but the carboxyl group is attached to one of the methyl groups. This acid exhibits an absorption in agreement with this view, and, moreover, appears to exist partly with its ring unbridged.

In conclusion we have to express our thanks to Mr. Foster Spoxton and to Dr. H. Bassett for the valuable help they have given us in the investigation.

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