58. *The Structure of Polyisoprenes. Part V. Ultra-violet Absorption Spectra of Certain Carbalkoxy-substituted* 1 : 5-*Dienes, and the Charge-resonance Spectra of Glutaconic Ester Enolate Ions.*

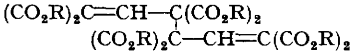
By L. Bateman and H. P. Koch.

Spectral evidence supports the conclusion reached in Part IV that ring-chain mesomerism in methyl and ethyl $\Delta^{1:5}$-hexadiene-1 : 1 : 3 : 3 : 4 : 4 : 6 : 6-octacarboxylates is non-existent in solution just as in the crystalline state. The data are not inconsistent with chain hyperconjugation in these molecules. The marked change in structural type that follows the addition of one molecule of hydrogen or hydrolytic reagent has been verified spectrographically.

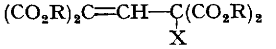
The spectra of methyl and ethyl $\alpha\gamma$-dicarboxyglutaconic esters and their sodium and cupric derivatives have been measured in various solvents, and tautomeric behaviour compared with that of other keto-enols. Of special interest is the intense long-wave absorption band of the enolate ions, which are recognised as simple structural analogues of the cyanine dyes giving rise to similar charge-resonance spectra. A preliminary comment is made on the present accepted structure of ethyl 6-ethoxy-α-pyrone-3 : 5-dicarboxylate.

It was pointed out in Part IV (preceding paper) that, both in empirical hypotheses and in the electronic theory of ring-chain mesomerism, double-bond interaction across space was thought to create a more saturated molecular condition which a short-wave shift in ultra-violet absorption would serve to reflect. Thus in the phorone series (this vol., p. 212) the normally unsaturated phorone is bright yellow, dibromophorone in which ring-chain mesomerism is postulated is only faintly coloured, and the saturated dicyclic bromohydroxyphorone is colourless.* Similar ring-chain mesomerism has been attributed to the octa-esters (I, R = Me or Et) in order to explain their peculiar chemical behaviour (Ingold, Parekh, and Shoppee, J., 1936, 142), but *X*-ray examination now shows that the methyl ester and almost certainly the ethyl ester do not possess *cis*-configurations in the crystalline state. Interspatial double-bond saturation is thus invalidated, but only by indirect arguments was it possible to extend the conclusion to conditions where the anomalous reactivity is actually observed. Spectrographic data were therefore required for two main reasons : (i) ring-chain mesomerism analogous to that envisaged in dibromophorone demands similar spectral consequences, and (ii) the molecular state in solution is directly investigated. In addition, the purity of preparative intermediates could be checked and it has been possible to confirm the basic structure assigned to certain derivatives.

(I.)



$$\begin{array}{l}(CO_2R)_2C{=}CH{-}C(CO_2R)_2\\ \qquad\qquad\quad\ \ |\\ (CO_2R)_2C{-}CH{=}C(CO_2R)_2\end{array}$$



$$(CO_2R)_2C{=}CH{-}\underset{X}{\underset{|}{C}}(CO_2R)_2$$

(II.)

The spectrographic approach is essentially a comparison of the octa-esters with a chemically normal analogue (II). However, of intrinsic interest to tautomeric and spectral theory is the rather complex spectroscopic and chemical behaviour of the $\alpha\gamma$-dicarbalkoxyglutaconic esters (II, X = H) and this is discussed separately in the second part of this paper.

Spectrographic Examination of the Octa-esters (*I*), *Some Derivatives, and Related Compounds.*—The ultra-violet absorption of the octaethyl ester (I, R = Et) had been examined qualitatively by Hartmann (*J. pr. Chem.*, 1911, **83**, 190) and adduced in support of the original bi*cyclo*butane formulation (cf. this vol., p. 212)—a conclusion definitely inacceptable in the light of the present work. Measurements in alcoholic solution of the octa-ethyl and -methyl esters, together with those of ethyl $\alpha\gamma$-dicarbethoxy-α-ethyl glutaconate (II, R = X = Et), are recorded in Fig. 1, where ε is plotted per tetra-ester residue. The absorption of all these compounds is very similar to that exhibited by the parent tetra-ester (II, R = Et, X = H) in hexane or acidified alcohol (see p. 217) and is typical of the normal $\overset{*}{C}{=}C{-}CO_2R$ chromophore, *e.g.*, crotonic acid,

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* Excluding the doubtful data of Müller and of Savard (cf. this vol., p. 211), it may be noted that the carbonyl chromophore is involved in all absorption anomalies of this type.

$CH_3·CH:CH·CO_2H$, has $\lambda_{max.}$ 2040 A., $\varepsilon = 12,000$ in alcohol (Hausser, Kuhn, *et al.*, *Z. physikal. Chem.*, 1935, *B*, **29**, 371). The absorption processes at the double bonds in the octa- and tetra-esters are evidently the same and, of special importance to the present problem, no absorption shift is apparent which is remotely comparable with that from phorone to dibromophorone. Support is thus derived for the arguments presented in the preceding paper that the non-existence of ring-chain mesomerism in the crystal applies equally to the dissolved state. Moreover, the correctness of the bi*cyclo*butane formula is rendered still less probable since conjugation of carbalkoxyl groups with a saturated, if strained, carbon nucleus would certainly be characterised by a distinct and less absorptive spectrum, as is the comparable *cyclo*propane conjugation (Carr and Burt, *J. Amer. Chem. Soc.*, 1918, **40**, 1590; Klotz, *ibid.*, 1944, **66**, 88).

The evidence was surveyed in Part IV which led Ingold, Parekh, and Shoppee to formulate the hexa-ester diacid derivatives as structural analogues of the octa-esters but, in contradiction to Guthzeit and Hartmann, to recognise a profound structural change on hydrolytic degradation. The absorption of the hexamethyl ester diacid can be compared in Fig. 1 with that of the acid-ester degradation product, the dihydro-octamethyl ester, and the octamethyl ester–methyl alcohol compound, three substances which, according to Ingold *et al.*, are related *cyclo*pentane derivatives. The large spectral difference fully supports the proposed change in structural type and, indeed, comparison with the saturated *cyclo*butane dimer of ethyl dicarbethoxyglutaconate (Fig. 1) and consideration of the actual intensity values leave no doubt that the structural change is from molecules with two double bonds, each conjugated with carbalkoxyl groups, to non-olefinic carbalkoxy-compounds.

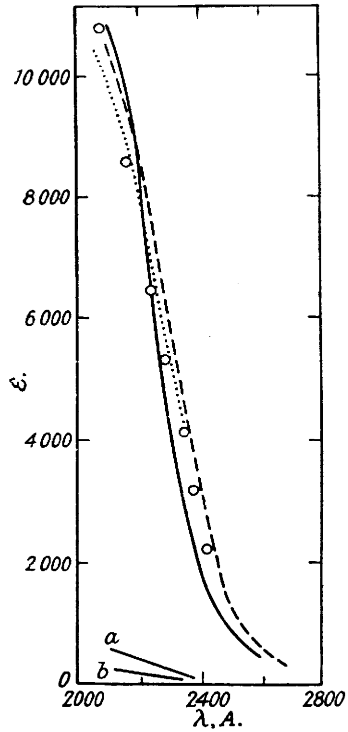


FIG. 1.

Spectra in ethyl-alcoholic solution.

———— *Ethyl αγ-dicarbethoxy-α-ethylglutaconate.*
— — — — *Octaethyl ester.*
.... *Octamethyl ester.*
○ ○ ○ *Hexamethyl ester di-acid.*
a *Ethyl* cyclo*butane octa-ester ; dihydro-octamethyl ester ; octamethyl ester–methyl alcohol compound.*
b *Hydrolytic degradation product* (*tetramethyl ester diacid*) (ε *per half-molecule*).

Normal substitutional influences seem inadequate to account for the chemical peculiarities of the octa-esters, and it has been suggested that the unique molecular condition is determined by chain hyperconjugation (this vol., p 213). It has already been shown (Bateman and Koch, J., 1944, 600) that the marked bond shortening in geranylamine hydrochloride, also attributed to chain hyperconjugation in 1 : 5-dienes, is not detectable by absorption in the quartz ultra-violet region. A similar interpretation of the chemistry of the octa-esters is compatible therefore with the spectral evidence, although its non-specificity precludes its use in a confirmatory sense.

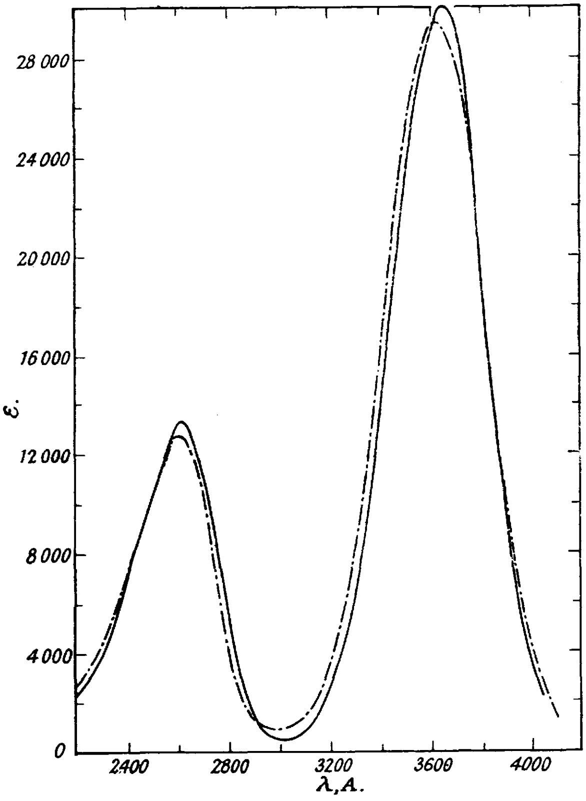
Spectra and Tautomerism of Glutaconic Acid Derivatives.—Stobbe and Wildensee (*J. pr. Chem.*, 1927, **115**, 163) studied the tautomeric behaviour in various solvents of ethyl αγ-dicarbethoxyglutaconate (II, R = Et, X = H) spectrographically, by the Hartley–Baly method, and by rough colorimetry with ferric chloride. The enol form, fully characterised by the sodio-derivative (X = Na), exhibited intense selective absorption at *ca.* **2600** A. and especially at *ca.* **3600** A., and these bands also appeared, though much more feebly, when the parent ester was dissolved in neutral ethyl alcohol. The alcoholic solution, however, did not obey Beer's law and the increased absorption intensity observed on dilution was recognised as a measure of increasing enol content. In ether, chloroform, hexane, or acidified alcohol, only fairly strong end absorption occurred, and if the α-carbon atom was ethylated (X = Et) similar but slightly greater end absorption resulted in either neutral or acidified alcohol or in hexane.

Our measurements on the pale yellow sodio-derivatives of the methyl and ethyl tetra-esters (II, X = Na, R = Me or Et) in ethyl-alcoholic solution are shown in Fig. 2. The corresponding green cupric derivatives have similar spectra in the ultra-violet (Fig. 3), but Beer's law is not obeyed. The absorption bands are displaced and less intense, but the curves suggest that at infinite dilution the spectra of the sodio-compounds will be exactly reproduced.

Neutral alcoholic solutions of the parent tetra-esters show the long-wave band of the respective sodio-derivatives at precisely the same wave-lengths, and the other band, although obscured by end absorption at the higher concentrations, is indicated by the inflection in the curves obtained from the more dilute solutions (Fig. 4). The intensity of these bands increases markedly on dilution, and if we assume that the pure enol form of the ester has the same absorption intensity as the sodio-compound, the equilibrium concentration of enol at the dilutions studied is readily calculated.

FIG. 2.

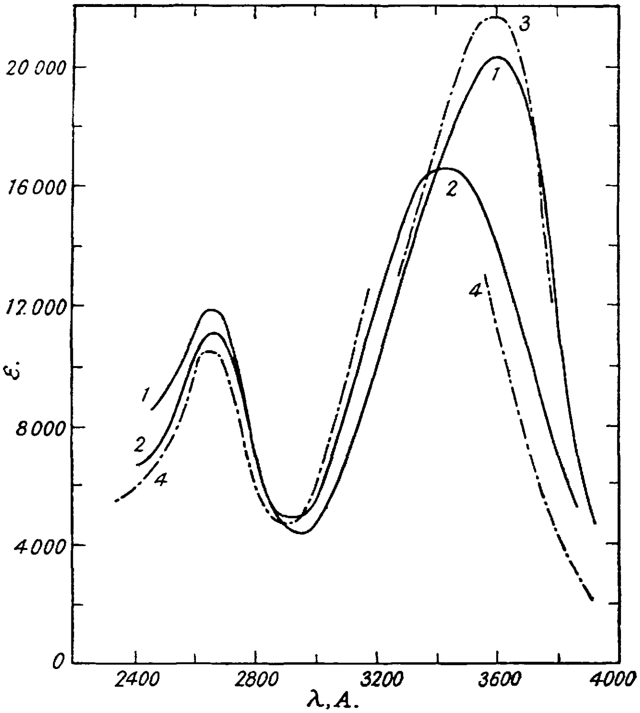
Sodio-derivatives of dicarbethoxyglutaconic esters in ethyl-alcoholic solution.



———— *Ethyl ester.* —.—.—.— *Methyl ester.*

FIG. 3.

Copper salts of dicarbalkoxyglutaconic esters in ethyl-alcoholic solution.

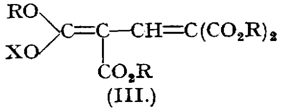


1. *Ethyl ester,* $[Cu^{++}] = 10^{-4}$ M.
2. ,, ,, ,, $= 5{\cdot}2 \times 10^{-4}$ M.
3. *Methyl* ,, ,, $= 3 \times 10^{-5}$ M.
4. ,, ,, ,, $= 7{\cdot}5 \times 10^{-4}$ M.

Ester.	Concn., M.	Intensity, ε.	Enol, %.
Tetramethyl	0·0103	170 ($\lambda_{max.}$ = 3630 A.)	0·6
,,	0·0004	3250	11
Tetraethyl	0·0125	135 ($\lambda_{max.}$ = 3660 A.)	$0{\cdot}4_5$
,,	0·0005	2350	8

In acidified alcohol, selective absorption disappears entirely (Fig. 4), and only end absorption corresponding to the $C{=}C{-}CO_2R$ chromophore is observed.

The classical enol formula (III, X = H) is inadequate to account for this varied behaviour, and the following points call for comment: (i) The free esters in neutral alcohol and their sodio-derivatives exhibit the same near ultra-violet absorption bands; (ii) the main enol band occurs at remarkably long wave-lengths; (iii) solutions of the copper derivatives show the enol bands displaced and of reduced intensity, but the full intensity at the usual wave-lengths is apparently developed at infinite dilution; (iv) solvent effects on the keto-enol equilibrium.



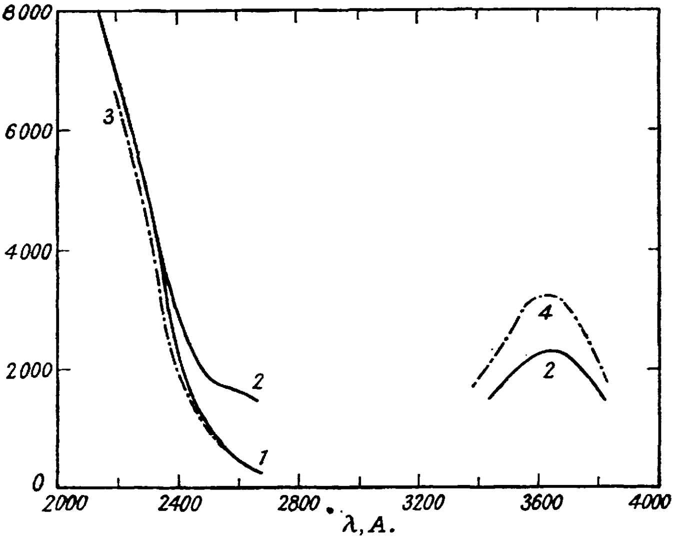
$(RO)(XO)C{=}C(CO_2R){-}CH{=}C(CO_2R)_2$

(III.)

(i) The first point implies that the hydrogen enol and its salt have the same electronic structure, in contrast to the enols of ketones such as ethyl acetoacetate, acetylacetone, etc., whose ionic salts always absorb more or less differently (at longer wave-lengths) and where it has been inferred that the salts possess somewhat different types of bonding (Hantzsch, *Ber.*, 1910, **43**, 3058; Morton, Hassan, and Calloway, J., 1934, 883).

FIG. 4.

αγ-Dicarbalkoxyglutaconic esters.



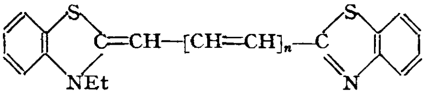
1. *Ethyl ester in* cyclo*hexane.*
2. ,, ,, ,, *alcohol* (5 × 10⁻⁴ M.).
3. *Methyl* ,, ,, 5% *alcoholic* H_2SO_4.
4. ,, ,, ,, *alcohol* (4 × 10⁻⁴ M.).

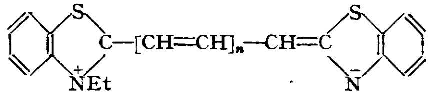
(ii) The structural factors governing the wave-length position of the first strong absorption band of conjugated compounds are now fairly well understood, mainly owing to the experimental work of Hausser and Kuhn on polyenes (*Z. physikal. Chem.*, 1935, *B*, **29**, 363, and following papers), and of Brooker on cyanine dyestuffs (*Rev. Mod. Physics*, 1942, **14**, 275).

Hausser and Kuhn and their collaborators found that the position of maximum absorption shifts to longer wave-lengths as n increases in the series $A—[CH{=}CH]_n—B$. In practice, absorption spectra of natural and synthetic polyenes of this type have often been employed as structural criteria since a reliable value of n can usually be deduced from $\lambda_{max.}$. The degree of conjugation present in the enol formulation (III) is similar to that of sorbic or muconic acid,

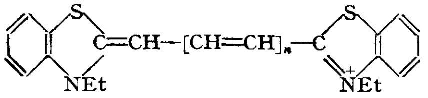
$$CH_3{\cdot}[CH{=}CH]_2{\cdot}CO_2H$$

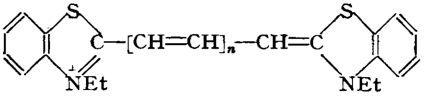
and $CO_2H{\cdot}[CH{=}CH]_2{\cdot}CO_2H$, which have $\lambda_{max.}$ 2540 and 2630 A., respectively (Hausser, Kuhn, *et al.*, *loc. cit.*, pp. 372, 383). Absorption beyond **3600** A. is not in fact observed until the homologue $CH_3{\cdot}[CH{=}CH]_5{\cdot}CO_2H$ is reached (*ibid.*, p. 403), so it is obvious that a structural condition other than, or additional to, ordinary conjugation is operative in the enols of the tetra-esters.

(IV.)




(V.)

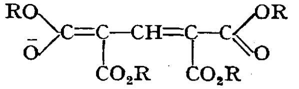
(VI.)




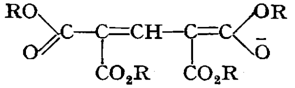
(VII.)

Brooker has pointed out that for compounds formally conjugated to the same extent, deepening of colour, as regards both λ and ε, is found in those structures which allow of effectively complete resonance degeneracy. The anhydro-base (IV), for example, is not fully mesomeric because the extreme canonical structure (V) is at a higher energy level. The corresponding ethiodide (VI) (a cyanine dye), of equal formal conjugation, is completely valency degenerate because the extreme alternative structure (VII) is now strictly equivalent, and this dye absorbs at considerably longer wave-lengths and also much more intensely than its parent base.

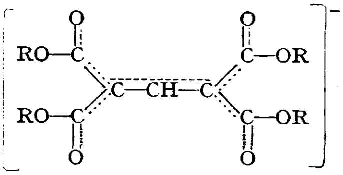
The enol ions of αγ-dicarbalkoxyglutaconic esters are clearly much simpler examples of the cyanine structural system, the two forms (VIII) and (IX) being energetically identical. All the ester groups will participate in the charge distribution, so the real state of the ion is as schematically shown in (X), in which six electrons are shared over the dotted tracks. This interpretation of the long wave-length absorption also throws light on the general behaviour of glutaconic ester-type tautomerides which, in short, is determined by the high stability of the enol anion.*



(VIII.)



(IX.)



(X.)

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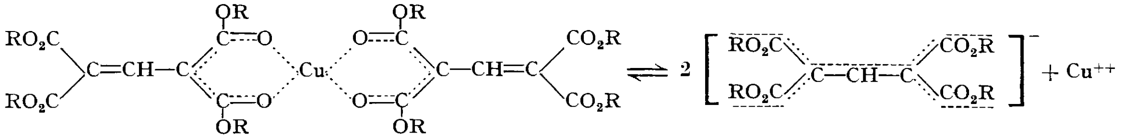
* The complete mesomerism of symmetrically substituted glutaconic acid derivatives, which is the basis of the "reversion to type," has been previously recognised in the chemical sense both implicitly and explicitly(Thorpe, Presidential Address, J., **1931**, 1002; Evans, Rydon, and Briscoe, J., **1939**, 1673). The structural relationship with the

(iii) The reduced absorption of solutions of the copper derivatives must be attributed to complex formation where co-ordination of the metal atom tends to localise the anionic charge in its neighbourhood. Two of the four extreme canonical structures will thus be preferentially stabilised, a process known to result in short-wave spectral displacement (Brooker, *loc. cit.*; Brooker and Sprague, *J. Amer. Chem. Soc.*, 1941, **63**, 3214). The equilibrium may be written :

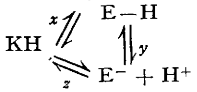


where reduced resonance in the chelated organic residue is compensated for by increased resonance in the metallic valencies.

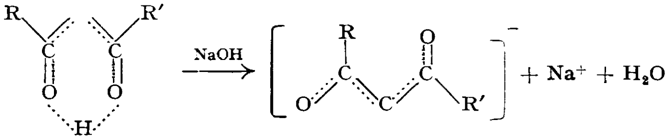
(iv) In ketones proper, enolisation is promoted by non-ionising solvents and repressed by hydroxylic solvents, *i.e.*, the reverse of the behaviour shown by the tetra-esters (II) which enolise exclusively in the latter media, and the equilibrium is not usually affected by dilution with the same solvent or by addition of acid (Morton and Rosney, J., 1926, 706; Morton, Hassan, and Calloway, *loc. cit.*; cf. however, Hantzsch, *loc. cit.*). Differences between these two tautomeric types, however, are not as fundamental as the solvent effects cursorily suggest.

The equilibrium in the glutaconic esters is represented by AH $\rightleftharpoons$ $A^- + H^+$, where AH and A^-, the keto-form and enol ion respectively, are the sole recognisable entities. There are no absorption bands corresponding to a third tautomer such as the undissociated enol. When A^- is sufficiently stabilised by resonance, enolisation will be promoted by proton acceptors to an extent depending on their basic strength, and inhibited completely by stronger acids and by aprotic solvents. The equilibrium is merely that of a simple acid–base system, where the energy of ionisation of the C–H bond is reduced by an amount approaching the resonance energy gained on enol-ion formation.

The position is less straightforward in ketones proper, since the hydrogen enol now has real existence. The equilibria are as shown in the inset, where KH, E–H, and E^- are the keto-form, enol, and enolate ion, respectively. The enol is energetically stabilised either by intramolecular (Sidgwick, J., 1925, **127**, 907) or, less commonly, by intermolecular (Hunter, *Chem. and Ind.*, 1941, **60**, 32) hydrogen bonding. In consequence, the chelated enols, in common with other hydrogen-bonded structures such as salicylaldehyde and *o*-hydroxyacetophenone, absorb at longer wave-lengths than their *O*-alkylated derivatives (Morton, Hassan, and Calloway, *loc. cit.*; Morton and Stubbs, J., 1940, 1354). Enol formation is favoured by conditions of minimum polarity; hydroxylic solvents, either by acting as alternative electron donors or by effecting charge distribution, inhibit severely. In the glutaconic esters, a hydrogen bridge across the 7-membered resonating unit (see X) is highly improbable stereochemically, while bonding within either malonic end group would interfere with full molecular mesomerism. Hence, the conditions for hydrogen enol stability are absent and in solvents such as hexane only the keto-structure exists.



Equilibrium (*z*) exactly simulates that described for the glutaconic esters. The absorption bands of the enol ions (E^-), exhibited by the sodium salts formed in water or alcohol (Morton *et al.*, *loc. cit.*), occur at longer wave-lengths and have much greater intensity than those of the chelated hydrogen enols. This is probably due to fuller mesomerism and to the setting up of a resonating charge (cf. Pauling, Gilman's " Organic Chemistry," 1938, p. 1888). The intensity increase may be further associated with the greater spatial elongation of the chromophore when the chelate ring is broken (cf. Koch, *Chem. and Ind.*, 1942, **61**, 273).



The position may be summarised thus : (*a*) In glutaconic esters, hydroxylic solvents and bases in general favour *enol-ion* formation; in aprotic solvents only the keto-form can exist. (*b*) In ketones proper, and malonic ester where chelation is similarly possible, *enol-ion* formation is favoured as in (*a*); aprotic solvents promote *hydrogen enol* formation.

Of further interest in the correlation of absorption spectra with structure in highly resonating systems is the spectrum of the so-called ethoxy-lactone (XI) obtained by loss of ethyl alcohol when attempts are made to distil ethyl αγ-dicarbethoxyglutaconate (see experimental section). With bands at 2500 and 3550 A. of practically identical intensity (Fig. 5), the spectrum in *cyclo*hexane is not dissimilar to the reported spectra of other α-pyrones (Haworth, Hirst, and Jones, J., 1938, 710; Haworth, Heslop, Salt, and Smith, J., 1944, 217), although

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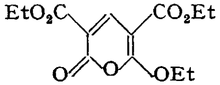
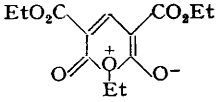
cyanines and the recognition of charge-resonance spectra in simple aliphatic systems have not been pointed out except in the paper of Schwarzenbach *et al.* (*Helv. Chim. Acta*, 1944, **27**, 576) which appeared after the completion of this work. The deductive approach of the Swiss authors presents a wider theoretical survey, but experimental corroboration is still limited. It is of interest that the sodium enolate of glutacondialdehyde is found to absorb intensely at 3650 A.

the intense near ultra-violet absorption is again notable. Guthzeit and Dressel (*Ber.*, 1889, **22**, 1413) found that the compound was decomposed by alcohol, but we have yet to obtain evidence that it exists at all in hydroxylic solvents. If dissolved in alcohol and immediately examined spectroscopically, only the original glutaconic ester can be detected, and this finds a parallel in the ferric chloride reaction which, entirely absent in *cyclo*hexane, becomes identical with that of the glutaconic ester on the addition of a few drops of alcohol. We suggest tentatively that the compound may really be the internal salt (XII). This symmetrical structure is highly degenerate in the distribution of the negative charge, and it follows that hydroxylic solvents will effect decomposition subsequent to internal ionic dissociation. Further pursuit of this topic awaits more extensive knowledge of the chemistry and spectroscopy of related lactones and their derivatives than it has yet been possible to obtain.

(XI.)

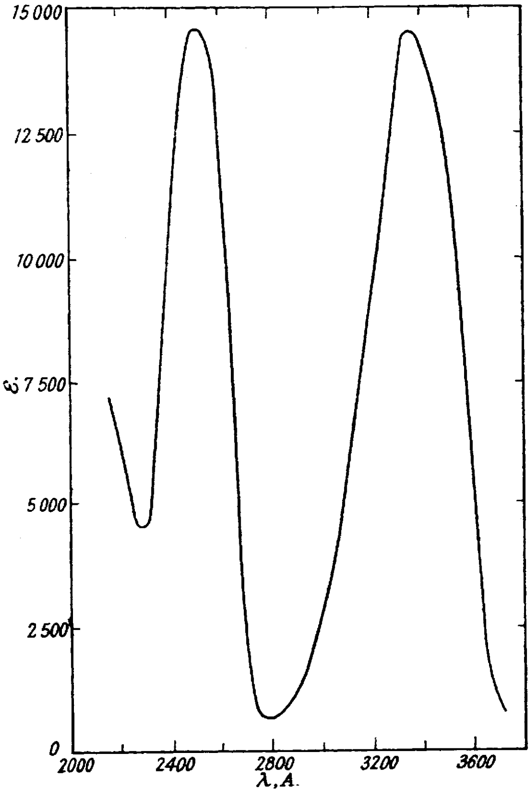




(XII.)

FIG. 5.

Lactone from ethyl dicarbethoxyglutaconate, in cyclo*hexane solution.*



EXPERIMENTAL.

The spectrographic technique was as detailed by Bateman and Koch (*loc. cit.*). Compounds not otherwise described were those employed for *X*-ray examination and are analytically specified in Part IV.

Sodio-tetra-esters (II, X = Na).—(i) The ethyl ester, prepared according to Ingold and Perren (J., 1921, 1582) and recrystallised four times from aqueous alcohol, had m. p. 260°. (ii) Guthzeit, Weiss, and Schaefer (*J. pr. Chem.*, 1909, **80**, 439) were unable to crystallise the crude methyl ester obtained from condensation of methyl sodiomalonate with chloroform, but describe an extraction procedure for isolating the pure sodio-derivative, m. p. 247—248°. We were unable to obtain pure specimens in this way (Found: C, 43·25; H, 4·4; Na, 8·4. Calc. for $C_{11}H_{13}O_8Na$: C, 44·5; H, 4·4; Na, 7·75%), although m. p.'s as high as 258—259° were observed. The pure compound was prepared by shaking the pure parent ester (II, R = Me, X = H; 2 g.) in ether with sodium carbonate (0·38 g.) in water, evaporating the aqueous layer under reduced pressure, extracting the residue with acetone, isolating the extract, and repeating the extraction. This solution yielded a very pale yellow powder, m. p. 264° (Found: C, 44·75; H, 4·4; Na, 7·5%).

Copper salts of the tetra-esters (II, X = ½Cu). (i) That from the ethyl ester, recrystallised three times from ethyl alcohol, had m. p. 177°. (ii) For the preparation of the *salt* from the methyl ester, an aqueous solution of the crude sodio-compound was treated with aqueous cupric sulphate, and the precipitate crystallised three times from ethyl alcohol, m. p. 246—248° [Found: C, 43·1; H, 4·35; Cu, 10·5. $(C_{11}H_{13}O_8)_2Cu$ requires C, 43·2; H, 4·3; Cu, 10·4%].

Dicarbalkoxyglutaconic Esters (II, X = H).—(i) *Ethyl ester.* Evaporation of the extract after decomposing the pure sodio-compound with dilute aqueous acid in the presence of ether gave a clear syrup (Found: C, 54·35; H, 6·75. Calc. for $C_{15}H_{22}O_8$: C, 54·5; H, 6·7%) whose spectrum was virtually identical with that of the pure crystalline methyl ester. As the usual distillation technique under reduced pressure causes decomposition with pyrone formation, short path, non-ebullioscopic, distillation between surfaces at 90° and − 78° at a pressure of 10^{-5} mm. of mercury was carried out. Even this distillate contained 3% of pyrone as estimated by the very sensitive spectroscopic method (Found: C, 54·55; H, 6·7%. Cf. analysis of the pyrone). (ii) *Methyl ester.* The recrystallised copper derivative, dissolved in chloroform, was shaken with dilute aqueous sulphuric acid until the organic layer became colourless. After being dried and evaporated under reduced pressure, the chloroform solution yielded a colourless syrup which eventually crystallised, m. p. 49°. Recrystallisation from ether–ligroin gave the pure ester, m. p. 50—51° (Found: C, 48·25; H, 5·15. Calc. for $C_{11}H_{14}O_8$: C, 48·2; H, 5·15%). Ingold, Parekh, and Shoppee give m. p. 43°. Submitted to non-ebullioscopic distillation (surface temperatures 80° and − 78°), the distillate in this case was free from pyrone and was spectrally identical with the pure crystals.

Pyrone (XI or XII).—The solid obtained on distillation of the ethyl tetra-ester under 11 mm. was recrystallised successively from ether and *cyclo*hexane and had m. p. 95° (Found: C, 54·9; H, 5·75. Calc. for $C_{11}H_{16}O_7$: C, 54·8; H, 5·6%).

Ethyl αγ-Dicarbethoxy-α-ethylglutaconate.—Prepared by Thole and Thorpe's method (J., 1911, **99**, 2187), this had b. p. 214°/25 mm. (Found: C, 57·0; H, 7·4. Calc. for $C_{17}H_{26}O_8$: C, 57·0; H, 7·3%). Selective absorption was entirely absent in *cyclo*hexane as well as in alcoholic solution. A fractionated specimen, b. p. 120—121°/0·05 mm., prepared according to Guthzeit and Dressel (*Ber.*, 1890, **23**, 3179), gave incorrect analyses (Found: C, 57·8, 58·0; H, 7·5, 7·6%) and reduced permanganate in acetone 10—15 times as rapidly as the pure compound but its absorption was only slightly greater. The nature of the impurity was not ascertained.

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