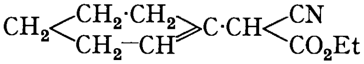
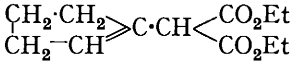
124. *Ethyl* Δ^1-cyclo*Pentenylmalonate.*

By G. A. R. Kon and Z. T. Ling.

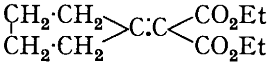
The improved technique which has lately been developed for partly or wholly arresting three-carbon tautomerism when an ester of the type $-CH{:}C\cdot CH(CO_2Et)_2$ is liberated from its sodio- or potassio-derivative (Kon and Nanji, J., 1931, 560; Gidvani, Kon, and Wright, J., 1932, 1027) has now been applied to the original examples studied by Hugh and Kon (J., 1930, 778), and the results confirm their conclusions. In particular, all attempts to prepare the βγ-form of ethyl α-cyano*cyclo*hexylideneacetate (ethyl α-cyano-Δ^1-*cyclo*hexenylacetate; I) have been fruitless; the preparation of ethyl *cyclo*pentenylmalonate (II) was, on the other hand, invariably successful.


$CH_2<\begin{matrix}CH_2\cdot CH_2\\ CH_2-CH\end{matrix}>C\cdot CH<\begin{matrix}CN\\ CO_2Et\end{matrix}$

(I.)

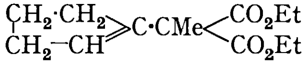

$\begin{matrix}CH_2\cdot CH_2\\ CH_2-CH\end{matrix}>C\cdot CH<\begin{matrix}CO_2Et\\ CO_2Et\end{matrix}$

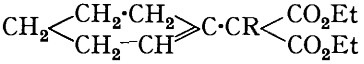
(II.)


$\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>C{:}C<\begin{matrix}CO_2Et\\ CO_2Et\end{matrix}$

(III.)

(IV.)


$\begin{matrix}CH_2\cdot CH_2\\ CH_2-CH\end{matrix}>C\cdot CMe<\begin{matrix}CO_2Et\\ CO_2Et\end{matrix}$


$CH_2<\begin{matrix}CH_2\cdot CH_2\\ CH_2-CH\end{matrix}>C\cdot CR<\begin{matrix}CO_2Et\\ CO_2Et\end{matrix}$

(V.)

Hugh and Kon were unable to estimate the amount of pure βγ-form (II) in the ester prepared by them, and in the absence of direct evidence we have endeavoured to answer the question indirectly.

The molecular refractions of the purest βγ-ester available, its αβ-isomeride (III), its α-methyl derivative (IV), and the corresponding *cyclo*hexane derivatives (V) have been determined by means of a Bellingham and Stanley critical angle refractometer; the new values are regarded as more accurate than those previously found.

Ester.	$[R_L]_D$.	Calc. from Eijkmann's value for ethyl malonate.	Δ.	*J*.
(II)	58·57	58·11	0·46	57·5
(IV)	62·93	62·73	0·20	43·3
(V, R = H), *a*	63·39	,,	0·66	23·5
,, ,*b*	63·13	,,	0·40	32·0
(V, R = Me)	67·47	67·35	0·12	42·7
(III)..................	59·70	58·11	1·59	0·1

The exaltation of the molecular refraction of ethyl *cyclo*pentenylmalonate (II) over that of its methyl derivative (IV, necessarily the βγ-compound) is only 0·26, compared with 1·39 for the pure αβ-ester (III) (the increment of 0·20 over the calculated value, found in the α-methyl ester, being deducted); it is assumed that the value for CH_2 is 4·62.

The exaltation is practically within the limits of experimental error, but the *maximum* αβ-content deduced from it is about 18%. The difference between the molecular refraction of the esters (IV) and (V, R = Me) is 4·54; if the same difference exists between (II) and (IV), the exaltation of (II) is even less.

Kon and Nanji's modified iodometric technique was applied to these esters and the results are in the last column of the table. The best specimen of the ester (II) had an addition of 57·5%, and the αβ-form had no measurable addition. It can be concluded that the minimum βγ-content of (II) is 57·5%, but the actual figure must be very much higher, because esters of this class react but sluggishly and incompletely with iodine chloride. For instance, the pure βγ-esters (IV) and (V, R = Me), which were examined in the hope of instituting a comparison, both have much lower additions of the order of 43%.

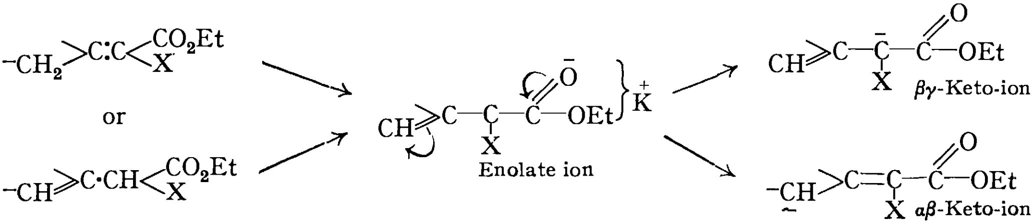
Ethyl *cyclo*hexenylmalonate should also be a pure βγ-ester, as it was prepared from the pure acid (compare Hugh and Kon, *loc. cit.*) through the silver salt. It shows an exaltation higher that that of the ester (II), but a second specimen (*b*), prepared by direct esterification of the acid with cold alcoholic hydrogen chloride, has a somewhat lower exaltation and a correspondingly higher iodine addition. This suggests that the specimen *a* cannot be the pure βγ-ester, in spite of the precautions taken in its preparation, and is therefore valueless as a standard of comparison with the ester (II). Judged from the optical data, the βγ-content of the specimen *b* should be of the same order as that of ethyl *cyclo*pentenylmalonate and we have not succeeded in raising it by regenerating the ester from its potassio-derivative; the low iodine addition of both specimens is certainly remarkable and is in agreement with our previous observations.

A comparison of the *cyclo*hexenyl ester with the ester (II) is particularly desirable, as it would help to eliminate the additional uncertainty due to the value for the CH_2 group; failing this, it appears hazardous to give an estimate of the βγ-content of the ester (II). From the optical data an approximate figure of 80% or more can be suggested, and this is consistent with the estimate based on iodine addition, since the addition of the pure ester would probably not exceed 70%; at the same time it is clear that the βγ-content of a given sample of (II) depends entirely on the conditions under which it is prepared and, not being an equilibrium value, would be subject to fluctuations, such as have actually been observed.

The value quoted by Baker and Bennett (*Ann. Reports*, 1931, **28**, 110), namely, 30—50% βγ, is based on a misunderstanding; this figure was given by Hugh and Kon (*loc. cit.*), not for the βγ-content, but for the *yield* of the relevant fraction of the ester.

It has again been noticed that the ester prepared by the esterification of pure *cyclo*pentylidenemalonic acid with cold alcoholic hydrogen chloride is mainly the βγ-ester; its βγ-content is much higher than that of the ester produced by the acidification of the potassio-derivative without special precautions ("equilibrium" ester). An attempt to obtain the pure βγ-ester by subjecting a mixture to reduction with aluminium amalgam, in the hope of converting the αβ-ester present into a bimolecular product, was unsuccessful.

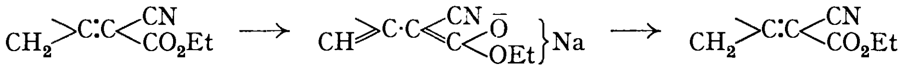
The following observations may be made with regard to the regeneration of esters of this type from their metallic derivatives. The formation of the latter must be regarded as an ionic process, because an atom of hydrogen is removed from the molecule and replaced by an atom of the metal. As in other similar cases, the anionic charge is presumably localised on oxygen and on acidification the enol should be produced. When hydrogen is reintroduced by the addition of water and acid, that is, under conditions favouring ionisation, the charge may be redistributed within the anion, and combination will then occur at the α-carbon atom, giving the βγ-form of the ester, and at the γ-carbon atom, producing the αβ-ester; the actual product formed will depend on the structure of the ester:



If the enolate is treated with a non-ionised polar molecule, such as an alkyl iodide, the redistribution of the charge proceeds as far as the α-carbon atom and the α-alkyl derivative is formed (it is immaterial from our point of view whether or not a small amount of the metallic derivative is present in the form of the *C*-compound in equilibrium with the *O*-form, and this then gives rise to the *C*-alkyl ester; the same arguments apply). In this reaction, the activation is not sufficient to bring about the redistribution of the charge in the three-carbon system, since no authenticated cases of γ-alkylation are known. In short, the ester behaves just like an ordinary monosubstituted malonic or cyanoacetic ester.

Finally, the action of a weak organic acid in a neutral solvent occupies an intermediate position; the activation may or may not be sufficient to bring about a redistribution of the anionic charge beyond the α-carbon atom. In comparatively inert compounds, such as the malonates considered in the present paper, the recombination takes place largely, if not entirely, in the α-position and the βγ-ester is formed. In the more mobile cyanoacetates, the activation is sufficient to bring about redistribution and the αβ-ester is formed if this happens to be the more stable form (*e.g.*, ethyl α-cyano*cyclo*hexylideneacetate); or a mixture is produced.

For this reason tautomerism, even in such compounds as those now discussed, is best considered as three-carbon, and not pentad keto-enol tautomerism as suggested by Shoppee (J., 1928, 2568; compare Ingold and Rothstein, J., 1929, 9). It is true that the system functions as a pentad *at times*—for instance, when an αβ-unsaturated cyano-ester passes into the sodio-derivative of the βγ-form and is then regenerated from it on acidification:



$$CH_2{>}C{:}C{<}{\begin{matrix}CN\\CO_2Et\end{matrix}} \longrightarrow \left.CH{\geqslant}C{\cdot}C{\leqslant}{\begin{matrix}CN\\C{<}{\begin{matrix}\bar{O}\\OEt\end{matrix}}\end{matrix}}\right\}Na \longrightarrow CH_2{>}C{:}C{<}{\begin{matrix}CN\\CO_2Et\end{matrix}}$$

The keto-enol system can, however, function independently of the three-carbon system, as in alkylation. In some cases enols or *aci*-forms are actually produced, as in some nitro-compounds (Fraser and Kon, this vol., p. 604) and rapidly revert to the original nitro-compound without any rearrangement of the electronic skeleton of the three-carbon system. At the opposite end of the scale may be placed pairs of αβ–βγ-isomerides, such as the diphenylpropenes (Ingold and Shoppee, J., 1925, **127**, 447), which are incapable of enolisation but nevertheless exhibit tautomerism; a large number of esters, nitriles, and ketones occupy an intermediate position.

Enolisation or, in other words, the capacity of the system as a whole to function as a pentad is thus not essential to tautomerism, although it frequently facilitates it.

EXPERIMENTAL.

Ethyl cyclo*Pentenylmalonate* (II).—*cyclo*Pentylidenemalonic acid (Kon and Speight, J., 1926, 2727) was kept with 5 vols. of (a) 2*N*- and (b) 0·7*N*-alcoholic hydrogen chloride at room temperature for a week, and the ester then isolated as usual. (a) gave an ester boiling mainly at 150°/17 mm., $d_{4°}^{18\cdot0°}$ 1·0549, n_D 1·4606,* iodine addition under Kon and Nanji's conditions (*loc. cit.*) 41·5, with a higher fraction of n_D 1·4641,* *J* 34·7. (b) gave an ester, b. p. 136°/10 mm., $d_{4°}^{18\cdot0°}$ 1·0570, n_D 1·46140, $[R_L]_D$ 58·75, *J* 44·9.

Regeneration from the potassio-derivative. 5·5 G. of potassium were dissolved in 42 c.c. of ethyl alcohol dried over metallic calcium, and the excess of alcohol was evaporated under reduced pressure at 100°. The residue was shaken with dry ether, and the evaporation repeated. The potassium ethoxide was covered with 200—300 c.c. of dry petroleum (b. p. 40—60°) and treated with 31·4 g. of the above ester, the separation of the potassio-derivative being facilitated by cooling in a freezing mixture and shaking, care being taken to exclude access of moisture throughout the operation. After an hour, the petroleum solution was decanted and the solid was washed three times with petroleum by decantation, until the washings were colourless. The solid was then covered with 250 c.c. of petroleum, cooled, and gradually treated with 17 g. of carefully dried benzoic acid in dry ether with shaking. After an hour, the solid, consisting of potassium benzoate and benzoic acid, was filtered off and the petroleum solution was washed with very dilute aqueous sodium carbonate and with water, dried, and evaporated. The

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* Rough values determined with a Pulfrich refractometer.

residue gave on distillation 9·2 g. of ester, b. p. 140°/15 mm., $d_{4°}^{15·7°}$ 1·05785, n_D 1·46030, $[R_L]_D$ 58·57, and *J* 57·3%. The petroleum washings obtained above were treated with dilute hydrochloric acid; the "equilibrium" ester recovered had b. p. 144°/14·5 mm., $d_{4°}^{18·5°}$ 1·05578, n_D 1·46257, $[R_L]_D$ 58·95, *J* 35·7%.

Reduction. 8 G. of the purest βγ-ester were treated with 8 g. of amalgamated aluminium foil (Harries and Eschenbach, *Ber.*, 1896, **29**, 380) covered with moist ether. When the reaction slackened after some 3 hours, a little water was added; finally, the ester was recovered; its iodine addition was 44%, and its refractive index had increased. When the "equilibrium" ester was treated in the same way, its iodine addition rose, but only very slightly. Treatment with aluminium amalgam evidently causes a conversion of the βγ- into the αβ-form in esters rich in βγ-.

Ethyl cyclo*Pentylidenemalonate* (III).—This was prepared by the esterification of the pure acid through the silver salt as described by Kon and Watson (J., 1932, 1) and had b. p. 138—141°/10 mm., $d_{4°}^{15·7°}$ 1·06728, n_D 1·47540, $[R_L]_D$ 59·70, *J* 0·05%.

*Ethyl α-Methyl*cyclo*pentenylmalonate* (IV).—Similarly prepared from the pure acid, this had b. p. 146°/11 mm., $d_{4°}^{18·8°}$ 1·04505, n_D 1·45993, $[R_L]_D$ 62·93, *J* 43·3%.

Ethyl cyclo*Hexenylmalonate* (V, R = H).—The ester prepared by the esterification of the acid through the silver salt had b. p. 150°/14 mm., $d_{4°}^{16·8°}$ 1·05454, n_D 1·46875, $[R_L]_D$ 63·39, *J* 23·5%. The specimen prepared by esterification with cold 2·2*N*-alcoholic hydrogen chloride as described on p. 598 had b. p. 154°/16 mm., $d_{4°}^{17·5°}$ 1·05072, n_D 1·46453, $[R_L]_D$ 63·13, *J* 32·0%.

Regeneration. This was carried out exactly as described on p. 598, except that the liberation of the "equilibrium" ester was carried out with benzoic acid. The potassio-derivative separated as a colourless solid, which could be filtered off; the ester obtained from it did not differ appreciably from the initial material in iodine addition and had $d_{4°}^{17·2°}$ 1·0516, n_D 1·4650, $[R_L]_D$ 63·13, whilst the specimen regenerated from the petroleum washings had $[R_L]_D$ 62·91. It is estimated that only one-third of the total potassio-derivative separates in the solid form.

*Ethyl α-Methyl*cyclo*hexenylmalonate* (V, R = Me).—The ester prepared through the silver salt had b. p. 155·5°/16 mm., $d_{4°}^{16·4°}$ 1·04827, n_D 1·46852, $[R_L]_D$ 67·47, *J* 42·7%.

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