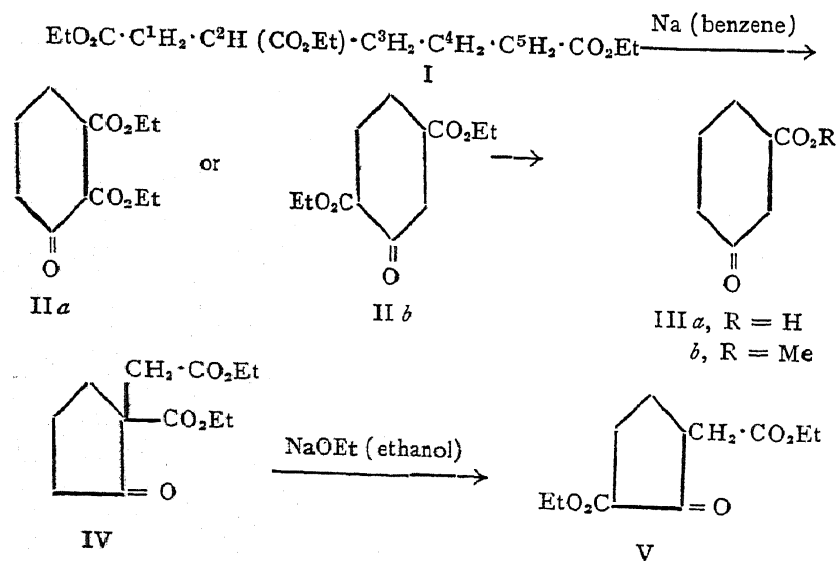# A PARADOXICAL CASE OF DIECKMANN CYCLISATION[1]

BY D. K. BANERJEE, F.A.Sc., J. DUTTA AND G. BAGAVANT

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PERKIN et al.[2] observed that the Dieckmann cyclisation of diethyl β-ethoxycarbonylpimelate (I) with sodium in benzene, followed by hydrolysis and decarboxylation, yielded 3-oxo*cyclo*hexanecarboxylic acid (III a), via β-keto-esters (II a and/or II b). Sen and Bagchi[3] proved that the Dieckmann product was mainly (II a). Ethyl 1-ethoxycarbonyl-2-oxo*cyclo*pentylacetate (IV) was isomerised by Chatterjee et al.[4] to ethyl 3-ethoxycarbonyl-2-oxo-*cyclo*pentylacetate (V), on treatment with an ethanolic solution of sodium ethoxide (1·1 mole). Following Openshaw and Robinson,[5] they suggested that the β-keto-ester (IV) underwent ring fission to form the triester (I) which cyclised to yield the diester (V).

$$EtO_2C \cdot C^1H_2 \cdot C^2H\ (CO_2Et) \cdot C^3H_2 \cdot C^4H_2 \cdot C^5H_2 \cdot CO_2Et \xrightarrow{\text{Na (benzene)}}$$

I

Chakravarti[1] explained the formation of (V) through an intra-molecular addition reaction of the mesomeric anion (VI a ⟷ VI b) which was formed by opening of the β-keto-ester (IV) with the ethoxyl ion. The proposed mechanism of ring closure is actually an interpretation of Nef's mechanism of the Claisen condensation[6] in terms of the electronic theory of valency, which, on the basis of Ingold's criticism of Nef's view,[7] is untenable. Further, the anion (VI a), in the presence of a large excess of ethanol, is likely to take

up initially a proton to form the triester (I), in which case, according to Chakravarti,[1] only the *cyclo*hexane-β-keto-ester (II a) should be formed. When the triester (I) was treated with ethanolic sodium ethoxide under Chatterjee's condition, the *cyclo*pentane-β-keto-ester (V) was formed as the major product.
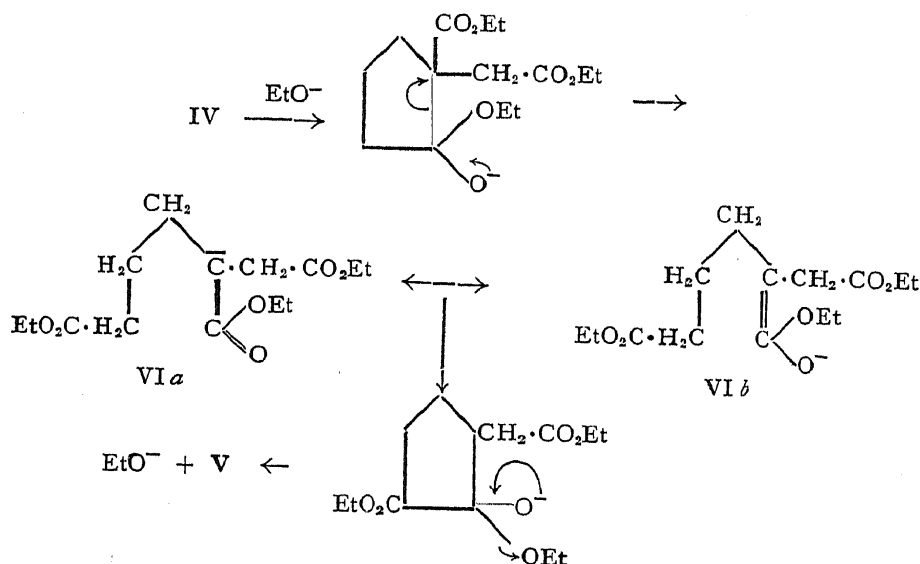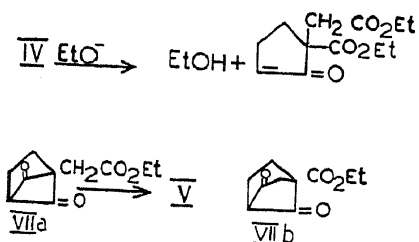

An explanation, not involving cleavage of the ring, is to assume ethyl-1-ethoxycarbonyl-2-oxo*cyclo*pentylacetate (IV) to undergo fission[8] in the presence of one molar quantity of sodium ethoxide in ethanol, yielding ethyl 2-oxo*cyclo*pentylacetate and diethyl carbonate which condense to yield (V). This, however, is unsatisfactory, as it involves an attack on the most hindered carbonyl group by the ethoxyl ion. Furthermore, β-keto-esters are formed in extremely poor yield during the condensation of ketones with diethylcarbonate in the presence of alcoholic sodium ethoxide.[9]
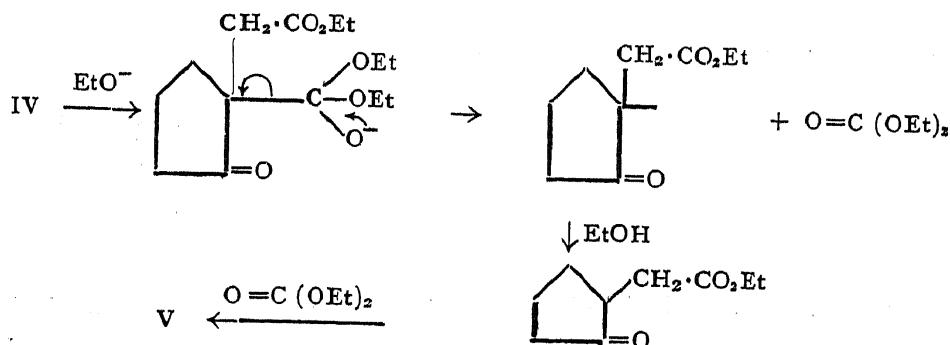

An alternative mechanism, which also dispenses with the formation of the anion (VI a), would be to assume the formation of a bicyclic (2 : 1 : 1-bi*cyclo*heptane) β-diketone intermediate (VII a) which opens up simulta-

neously with, or after, its formation to yield (V). But this also is not feasible as there is no *a priori* reason to assume its preferential formation to that of the more stable 2:1:2-bi*cyclo*octane derivative (VII *b*). It has been observed experimentally that ethyl 1-ethoxycarbonyl-2-oxo*cyclo*pentylacetate (IV), on treatment with sodium ethoxide in benzene, undergoes conversion to the *cyclo*hexane compound.

IV $\underset{\longrightarrow}{EtO^-}$ EtOH + [structure: CH$_2$CO$_2$Et, –CO$_2$Et, =O]

[structure VIIa: CH$_2$CO$_2$Et, =O] $\rightleftharpoons$ V [structure VIIb: CO$_2$Et, =O]

In order to find out whether the anion (VI *a*), resulting from an open chain system, would also yield the *cyclo*pentanone derivative (V), diethyl β-acetyl-β-ethoxycarbonylpimelate was treated according to Chatterjee's conditions. In this case, an attack of the ethoxyl ion on the carbonyl of the acetyl group was expected to yield the anion (VI *a*) and ethyl acetate. The reaction product had a strong smell of ethyl acetate and gave a deep colour with ferric chloride. The β-keto-ester fraction, on hydrolysis and decarboxylation, yielded a keto-acid identified as 2-oxo*cyclo*pentylacetic acid (VIII *a*), thus indicating that the anion (VI *a*) can yield the *cyclo*pentanone system (V) under the conditions employed.

[reaction scheme]
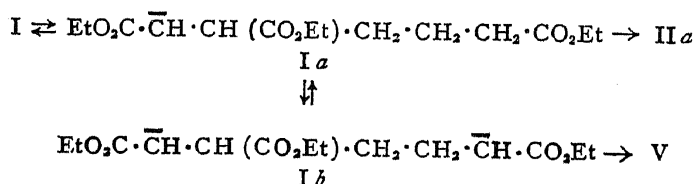
VIII *a*, R = H
b, R = Me
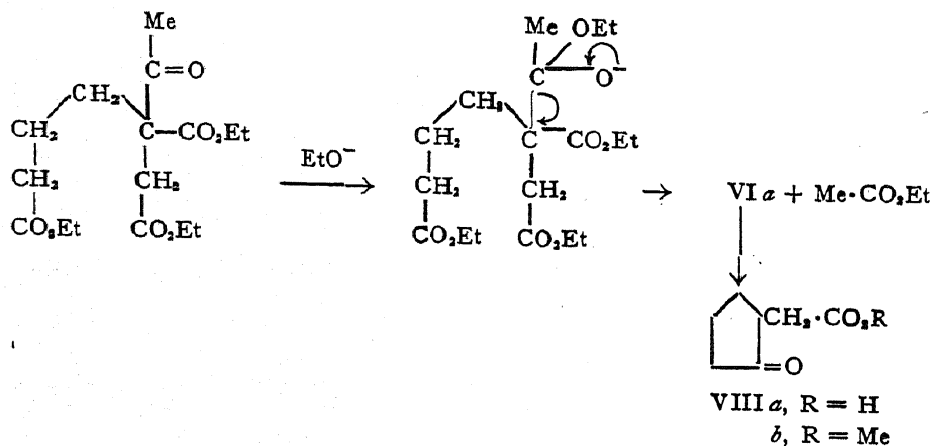
It was found that the treatment of (IV) with one-quarter mole of sodium ethoxide in ethanol produced the triester (I) in 75% yield, together with a small quantity of a β-keto-ester* which has been found to be mainly the

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* We are indebted to Mr. P. Bagchi of the Association for the Cultivation of Science, Calcutta, for bringing to our notice the formation of a β-keto-ester in this reaction.

*cyclo*hexane derivative (II *a*). Treatment of the triester (I) with one or two moles of sodium ethoxide in benzene gave the *cyclo*hexane-β-keto-ester (II *a*) in good yield.

The aforementioned experimental facts suggest that the formation of the *cyclo*hexanone or the *cyclo*pentanone derivative depends on the amount of available ethoxyl ion. In benzene medium, as well as when one-quarter mole of sodium ethoxide in ethanol is used, due to the low concentration of ethoxyl ion, a proton is abstracted preferentially from the most acidic (C_1) of the methylene and methine groups, which, in the triester (I), is the one constituting a part of the succinic ester residue (*cf.* Chakravarti[1]), thus producing the anion (I *a*) which yields (II *a*) as the cyclised product. In the presence of an ethanolic solution of an excess of sodium ethoxide, the formation of a bianion (I *b*), even in traces, seems to explain satisfactorily the observed facts. In (I *b*) due to the presence of negative charges at C_1 and C_5, the carbonyl activity of the ethoxycarbonyl groups attached to these carbon atoms is reduced, leaving that of the ethoxycarbonyl group attached to the C_2-carbon atom strongest, so that the reaction of the C_2-ethoxycarbonyl with the C_5-anion furnishes the *cyclo*pentane-β-keto-ester (V). However, the existence of a highly energetic bianion of the type (I *b*) appears improbable.

$$I \rightleftarrows EtO_2C \cdot \overline{C}H \cdot CH \, (CO_2Et) \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CO_2Et \rightarrow II\,a$$
$$I\,a$$
$$\Updownarrow$$
$$EtO_2C \cdot \overline{C}H \cdot CH \, (CO_2Et) \cdot CH_2 \cdot CH_2 \cdot \overline{C}H \cdot CO_2Et \rightarrow V$$
$$I\,b$$

The cyclisation products in these experiments were characterised through the derivatives of the keto-acids (III *a* and VIII *a*) obtained by hydrolysis and decarboxylation of the β-keto-esters (II *a* and V). By this procedure identification of only the major product could be strictly claimed. The purity of the keto-esters (III *b* and VIII *b*) was therefore investigated by infra-red spectra and authentic samples of (III *b* and VIII *b*) required for this purpose were prepared; the former by the addition of hydrogen cyanide to *cyclo*hexen-3-one followed by treatment of the resulting keto-nitrile with methanolic hydrogen chloride, and the latter by the method of Linstead and Meade.[10]

The infra-red spectra revealed that none of the samples was absolutely pure. The intensity distribution in a spectral line being Gaussian, the observed intensity due to overlap of the two lines at 1740 cm.$^{-1}$ (*cyclo*pentanone carbonyl) and at 1720 cm.$^{-1}$ (*cyclo*hexanone carbonyl) could be

uniquely resolved into the two respective Gaussian curves. On this basis percentage compositions of the mixtures were calculated.

The spectra of samples obtained from the triester (I) and the keto-diester (IV), by treatment according to Chatterjee's conditions, were found to be identical, indicating the presence of ca. 90% of methyl 2-oxocyclopentyl-acetate (VIII b). This indicates the possibility of the triester (I) being an intermediate (vide antea) in the transformation of (IV) to the isomerised β-keto-ester (V).

The spectra of samples, obtained from (I) by treatment according to Perkin's[2] conditions and with sodium ethoxide in benzene, and from the diester (IV) by treatment with one-quarter mole of sodium ethoxide in ethanol, showed that these consisted mainly of methyl 3-oxocyclohexane-carboxylate (III b); the first two samples were very similar and contained ca. 80% of (III b).

Recent kinetic studies[11, 12] indicated agreement with the accepted mechanism[7] of Dieckmann cyclisation being composed of four stages (1–4). Reed and Thornley[11] showed that the reaction, in an ethanolic solution of an excess of sodium ethoxide, was reversible and unimolecular, and that the
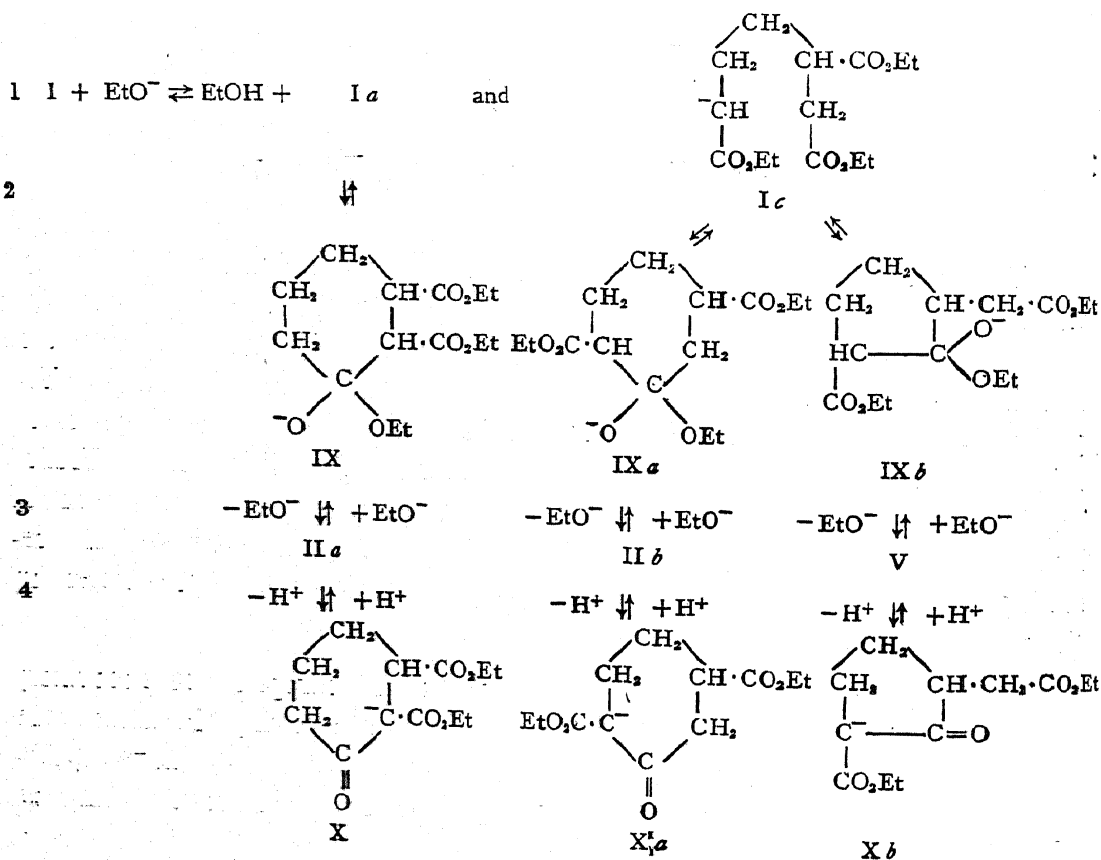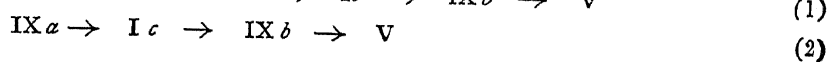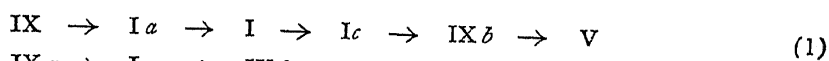
second step was rate-determining.[12] The English workers also showed that this reaction, in a solvent of low dielectric constant and a high concentration of sodium ethoxide, was bimolecular and that the first step was rate-determining. They also provided some evidence for the existence of steric retardation.

Various courses, which the Dieckmann cyclisation of the triester (I) can follow, have been indicated in the chart, and these involve two reactive methylene groups at C_1 and C_5 in (I). The particular case where the anion (VI a) is formed by removal of the proton from the C_2-carbon atom has not been considered, because the third step in this case should give rise to a β-keto-ester without an enolisable hydrogen, thus rendering its isolation from the equilibrium mixture impossible.[13] Although, for reasons mentioned before, the carbanion (I a) is expected to be formed predominantly, yet the formation of a small quantity of the carbanion (I c) along with the former is always possible. The results obtained under different conditions of Dieckmann reaction in the present case may be interpreted on the basis of these considerations and the findings of the aforementioned kinetic studies.[11, 12]

A. *Treatment of Diethyl β-Ethoxycarbonylpimelate* (*I*) *with Sodium* (*Two Moles*) *or Sodium Ethoxide* (*One or Two Moles*) *in Benzene.*—Under these conditions the reaction is bimolecular[11] and the triester (I) should yield predominantly the anion (I a) and traces of the anion (I c) (*vide antea*). As the second step is faster than the first (the rate-determining step[11]), conversion of the anion (I a) to the cyclised anion (IX) will be faster than its formation, and thus it will be continuously removed. This coupled with the low solubility of the sodium salt[12] of (X) in benzene make the Dieckmann reaction yield (II a) as the major product. Small quantities of β-keto-esters (II b and V) should also be produced from the anion (I c).

B. *Treatment of* (*I*) *or Ethyl* 1-*Ethoxycarbonyl-2-oxocyclopentylacetate* (*IV*) *with Sodium Ethoxide* (1·1 *Mole*) *in Ethanol.*—In this case the reaction is unimolecular,[11] and the second step is rate-determining[11, 12] and therefore slower than the first, thus resulting in the accumulation of the anions (I a and I c). All steps are reversible, and the presence of a large quantity of ethanol facilitates the formation of the neutral ester (I) from the anions, so that the transformation of the anions (IX and IX a) to the *cyclo*pentane-β-keto-ester (V) is possible through the following sequences:

$$\text{IX} \rightarrow \text{I}a \rightarrow \text{I} \rightarrow \text{I}c \rightarrow \text{IX}b \rightarrow \text{V} \tag{1}$$

$$\text{IX}a \rightarrow \text{I}c \rightarrow \text{IX}b \rightarrow \text{V} \tag{2}$$

Reed and Thornley[11] found that an α-alkyl substituent causes steric retardation in the ring fission. In the β-keto-esters (II a, II b and V), α-substi-

tuents to the keto group are most bulky in (V), thus creating maximum hindrance in the approach of the ethoxyl ion and making the third step comparatively more irreversible in this case than in others.

The loss of a proton, in the fourth step, from the β-keto-esters (II a, II b, and V) changes the co-ordination number of the involved carbon atoms from four to three. Such a change is aided in and opposed by five-membered and six-membered ring systems respectively,[14, 15] resulting in the *cyclo*pentane derivative being comparatively more acidic and hence existing predominantly in the equilibrium mixture.

Brown *et al.*[14] have shown that exocyclic and endocyclic double bonds are preferred by five-membered and six-membered ring systems respectively. The canonical structure of the enolate ion (synion S), formed in the last step, suggests that the mesomeric anion should possess considerable exocyclic double bond character,† and thus be more stable in the case of the *cyclo*pentanone anion (X b).
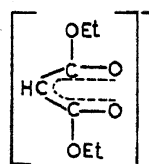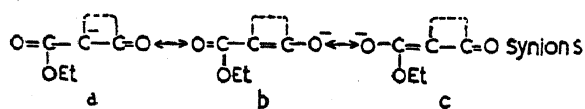
XI

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† Russel,[15] in explaining the higher enolisation of *cyclo*-hexanone compounds compared to *cyclo*pentanone derivatives pointed out that in the equilibrium mixture (*vide infra*) the form c' would be subordinate when R is OEt, since diethyl malonate does not enolise appreciably (Gero, *J. Org. Chem.*, 1954, 19, 1961).
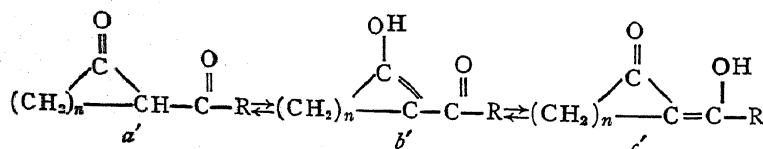

Bender and Figueras (*J. Amer. Chem. Soc.*, 1953, 75, 6304) have shown in the infra-red study of the "enolate ion" that in β-keto-ester and β-diketone systems the ester and ketonic carbonyl bands practically vanish to give "enolate ion" band(s). The infra-red study of diethyl malonate anion establishes that it is best represented by (XI) in contrast to the structure of diethyl malonate, so that the contribution of the form (c) in the (synion S) should be considerable.

Thus due to the greater acidity and higher stability of the *cyclo*pentanone system, and the comparative irreversibility of the third step in the formation of (V), the triester yields the *cyclo*pentane-β-keto-ester (V), as the major product, under Chatterjee's conditions.

It is now proposed that the keto-diester (IV), under these conditions, first yields the anion (VI *a*)[1] which, in the presence of a large amount of ethanol, takes up a proton to form the triester (I), finally to yield (V) as the major product.

The aforementioned arguments were conclusively proved by treating ethyl 2-oxo*cyclo*hexane-1 : 2-dicarboxylate (II *a*)[2] under Chatterjee's conditions and obtaining thereof ethyl 3-ethoxycarbonyl-2-oxo*cyclo*pentylacetate (V), which on hydrolysis, decarboxylation, and subsequent esterification yielded a sample of methyl 2-oxo*cyclo*pentylacetate (VIII *b*) having an infra-red spectrum identical with those of the products obtained from (I) or (IV) by a similar procedure.

C. *Treatment of* (*I*) *with One-Quarter Mole of Sodium Ethoxide in Ethanol.*—In this case, in the β-keto-ester fraction, the *cyclo*hexane-β-keto-ester (II *a*) was predominantly formed, but the infra-red spectrum showed that the *cyclo*pentane-β-keto-ester (V) was present in comparatively larger quantity than when (I) was treated with sodium ethoxide in benzene (*vide antea*). According to the equilibrium nature of the reaction, however, the β-keto-ester (V) ought to have been formed preponderantly also in this case. It was therefore concluded that sufficient time had not been allowed for attainment of the equilibrium of the reaction mixture in the presence of low concentration of ethoxyl ion, and this was confirmed when the reaction mixture was heated for a prolonged period to yield (V) as the major product in the β-keto-ester fraction. This observation is not in agreement with the bianion theory.
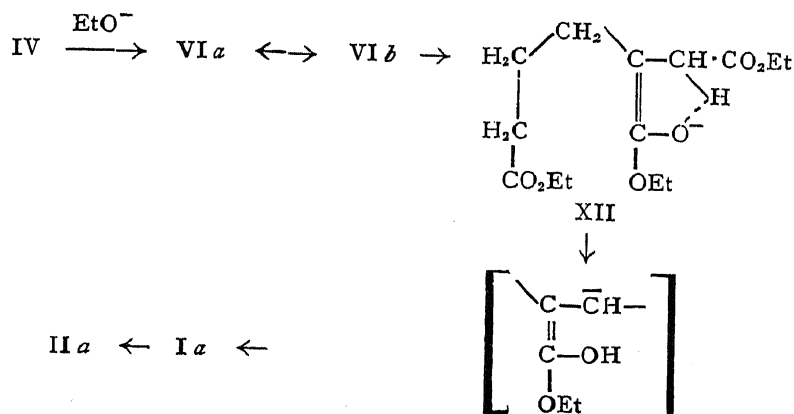
D. *Treatment of* (*IV*) *with Sodium Ethoxide in Benzene.*—The formation of the *cyclo*hexane system in this case may be assumed to proceed through the mesomeric anion (VI $a \longleftrightarrow$ VI b),[1] followed by conversion to the anion (I a) *via* the hydrogen-bonded intermediate (XII).

EXPERIMENTAL

Ethyl 1-*Ethoxycarbonyl*-2-*oxocyclopentylacetate* (*IV*).—This was prepared by the method of Chatterjee *et al.*[4] The treatment of the sodio-derivative of ethyl 2-oxo*cyclo*pentanecarboxylate, formed by the Dieckmann cyclisation of diethyl adipate, *in situ* with ethyl chloroacetate under refluxing conditions yields mainly diethyl β-ethoxycarbonylpimelate, b.p. 153–158°/0·8 mm., n_D^{23} 1·4390, together with a small quantity of a β-keto-ester fraction, b.p. 118–123°/1 mm.

2-*Oxocyclopentylacetic Acid* (VIII a).—This was obtained adopting the procedure of Linstead and Meade,[10] m.p. 52° (lit.[10], m.p. 53°), semicarbazone m.p. 198° (lit.[4], m.p. 198°). The 2 : 4-*dinitrophenylhydrazone* was prepared by the perchloric acid method[16] and crystallised from dilute acetic acid, m.p. 215–216° (decomp.) (Found: N, 17·44. $C_{13}H_{14}O_6N_4$ requires N, 17·39%). The *methyl ester* (VIII b) was prepared using methanol and sulphuric acid, b.p. 94–96°/0·8 mm. (Found: C, 61·42; H, 7·81. $C_8H_{12}O_3$ requires C, 61·54; H, 7·69%).

When the β-keto-ester (purified through alkali extraction) obtained from ethyl 1-ethoxycarbonyl-2-oxo*cyclo*pentylacetate (IV) by the procedure of Chatterjee *et al.*[4] was hydrolysed, decarboxylated, ·and subsequently esterified with methanol and sulphuric acid, a sample containing about 90% of methyl 2-oxo*cyclo*pentylacetate (VIII b) (*vide* Fig. 3) was obtained.

3-*Cyanocyclohexanone.*—To a stirred and cooled (ice and salt) solution of *cyclo*hexen-3-one[17] (9·6 g.) and glacial acetic acid (6 ml.) in rectified spirit (80 ml.) was added an aqueous solution of potassium cyanide (13 g. in 38 ml.) in course of 35 min., and it was allowed to stand overnight at 0°. After the addition of brine (150 ml.), the nitrile was thoroughly extracted with ether. The combined ethereal extract was washed with brine and dried (Na_2SO_4). The residue, after removal of the solvent, was fractionated to yield the *nitrile* (5·4 g.), b.p. 149–150°/17 mm. (Found: N, 11·11. C_7H_9ON requires N, 11·38%). The *semicarbazone* was crystallised from rectified spirit, m.p. 177–178° (Found: N, 31·15. $C_8H_{12}ON_4$ requires N, 31·11%). The 2 : 4-*dinitrophenylhydrazone*, prepared by the perchloric acid method, was crystallised from ethyl acetate-alcohol, m.p. 205° (Found: N, 23·12. $C_{13}H_{13}O_4N_5$ requires N, 23·12%).
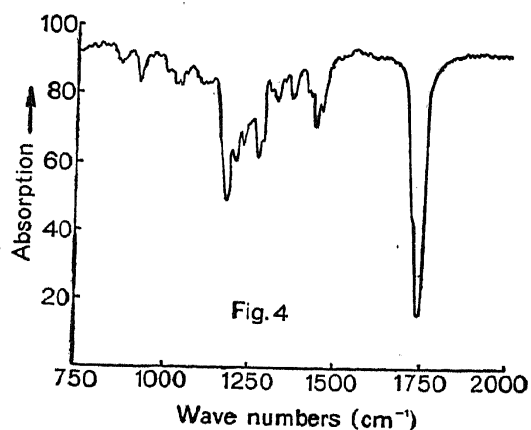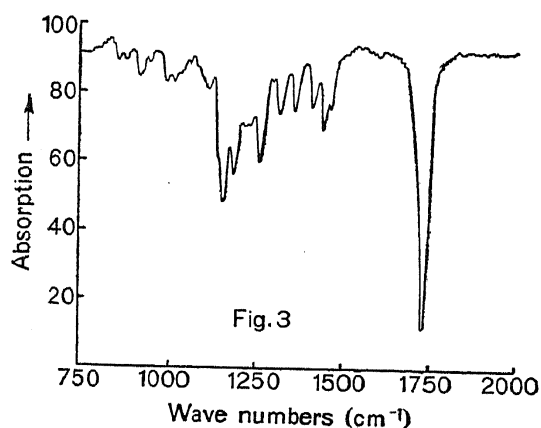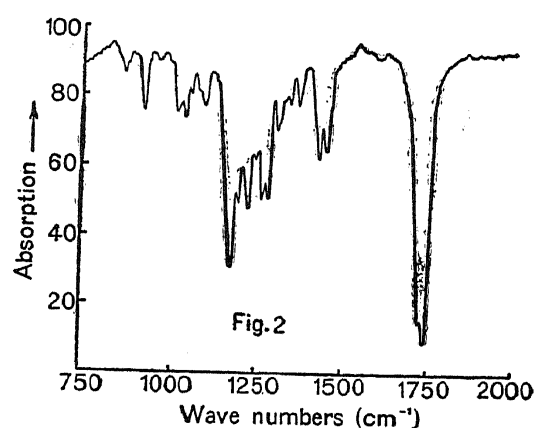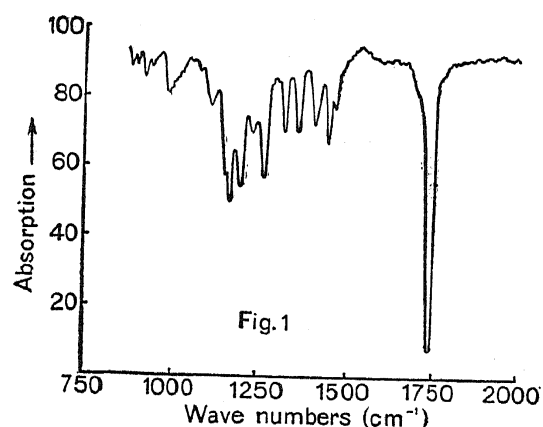
FIG. 1. Methyl 2-oxo*cyclo*pentylacetate.

FIG. 2. Methyl 3-oxo*cyclo*hexanecarboxylate.

FIG. 3. Keto-ester obtained under Chatterjee's conditions from Ethyl 1-ethoxycarbonyl-2-oxo*cyclo*pentylacetate.

FIG. 4. Keto-ester obtained under Perkin's conditions from Diethyl β-ethoxycarbonylpimelate.

Methyl 3-Oxocyclohexanecarboxylate (III b).—To a cooled (ice and salt) solution of the aforementioned nitrile (2·7 g.) in dry methanol (10 ml.) was added anhydrous methanol (35 ml.) saturated with dry hydrogen chloride at 0°. After allowing it to stand for 2 hr. in the freezing mixture and over-night in a refrigerator, the mixture was refluxed for 10 hr. After removal of a part of the methanol, brine was added to the cooled mixture, and it was worked up in the usual manner to yield *methyl 3-oxocyclohexanecarboxylate* (III *b*) (1·02 g.), b.p. 121–123°/16 mm., n_D^{24} 1·4590 (Found: C, 61·2; H, 7·7. $C_8H_{12}O_3$ requires C, 61·5; H, 7·69%). The *semicarbazone* was crystallised from aqueous methanol, m.p. 168° (Found: N, 19·33; $C_9H_5O_3N_3$ requires N, 19·72%). 3-Oxo*cyclo*hexanecarboxylic acid was prepared by hydrolysis of the ester with 6 N-hydrochloric acid. The 2 : 4-*dinitrophenylhydrazone* of this acid, obtained by the perchloric acid

method, was crystallised from ethyl acetate, m.p. 202° (Found: N, 17·27. $C_{13}H_{14}O_6N_4$ requires N, 17·39%).

When the β-keto-ester obtained from diethyl β-ethoxycarbonylpimelate (I) by the method of Dobson, Ferns and Perkin[2] was hydrolysed, decarboxylated, and subsequently esterified with methanol and sulphuric acid, a sample containing about 80% of methyl 3-oxo*cyclo*hexanecarboxylate (III *b*) (*vide* Fig. 4) was obtained.

Diethyl β-Acetyl-β-ethoxycarbonylpimelate.—Diethyl α-acetyladipate (13 g.) was added dropwise to a cooled (ice) and stirred suspension of potassium (2·2 g.) in toluene (50 ml.), and the mixture allowed to stand overnight at the room temperature. The potassio-derivative, thus formed, was heated under reflux for 12 hr. with ethyl bromoacetate (10 g.). The product, on fractionation, yielded diethyl β-acetyl-β-ethoxycarbonylpimelate (8·6 g.) as a colourless oil, b.p. 165–170°/1 mm. (Found: C, 58·4; H, 8·33. Calc. for $C_{16}H_{26}O_7$: C, 58·2; H, 7·94%).

Treatment of Diethyl β-Acetyl-β-ethoxycarbonylpimelate with Sodium Ethoxide under Chatterjee's[4] Conditions.—To a solution of sodium ethoxide, prepared from sodium (0·4 g.) in dry ethanol (7 ml.), was added diethyl β-acetyl-β-ethoxycarbonylpimelate (6·1 g.), and the mixture refluxed for 8 hr. The reaction product, which had a strong smell of ethyl acetate, was acidified to Congo red with iced hydrochloric acid and extracted with ether. The extract was washed with brine, sodium hydrogen carbonate solution, and water successively, and distilled to yield a colourless liquid (1·73 g.), b.p. 132–137°/1 mm., which gave a deep colour with alcoholic ferric chloride. This was refluxed for 24 hr. with a mixture of acetic acid (5·3 ml.), hydrochloric acid (2·2 ml.), and water (1·5 ml.). The reaction mixture was distilled to give a solid, m.p. 50–53°. The semicarbazone and 2:4-dinitrophenylhydrazone melted at 196° and 215–217° respectively; mixed melting points with authentic semicarbazone and 2:4-dinitrophenylhydrazone of 2-oxo*cyclo*pentylacetic acid respectively were not depressed.

Treatment of (a) Diethyl β-Ethoxycarbonylpimelate (I) and (b) Diethyl 3-Oxocyclohexane-1:2-dicarboxylate (II a)[2] with Alcoholic Sodium Ethoxide under Chatterjee's Conditions.—The β-keto-esters (purified through alkali extraction), obtained from these experiments, were hydrolysed, decarboxylated, and esterified with methanol and sulphuric acid, when samples of keto-esters having infra-red spectra identical with Fig. 3 were obtained.

Treatment of Ethyl 1-Ethoxycarbonyl-2-oxocyclopentylacetate (IV) with One-Quarter Mole of Sodium Ethoxide in Ethanol.—(a) To a solution of

sodium ethoxide, from sodium (1·4 g., 0·06 mole) and ethanol (11·1 g., 0·24 mole), was added the diester (IV) (59·0 g., 0·24 mole), and the mixture was heated for 3 hr. on a steam-bath. The crude product (65·8 g.), obtained after acidification and extraction with ether, gave a deep purple colour with alcoholic ferric chloride. It was dissolved in ether, and the β-keto-ester was removed by repeated extraction with cold, 5% aqueous sodium hydroxide. The ethereal solution, on distillation, yielded diethyl β-ethoxycarbonyl-pimelate (I) (52·8 g.), b.p. 158–160°/1 mm., which gave a faint colour with ferric chloride. To obtain the pure triester (I), this was hydrolysed, and esterified with ethanol-sulphuric acid, and then the product could be easily fractionated from the considerably lower boiling keto-monoesters (III R = Et; and VIII R = Et).

The alkaline extract was acidified with ice and hydrochloric acid and thoroughly extracted with ether. The ether extract, after being washed with sodium hydrogen carbonate solution and water, was dried, and then distilled to give a colourless oil (4·8 g.), b.p. 125–135°/1 mm. A redistilled portion b.p. 125–127°/0·8 mm. was analysed (Found: C, 59·51; H, 7·32. Calc. for $C_{12}H_{18}O_5$: C, 59·51, H, 7·44%).

The aforementioned β-keto-ester was hydrolysed and decarboxylated by the usual procedure. The crude 2:4-dinitrophenylhydrazone, m.p. 170–195°, of the resulting product, after two crystallisations from ethyl acetate-light petroleum (40–60°), melted at 202°; the mixed melting point with the 2:4-dinitrophenylhydrazone of 3-oxo*cyclo*hexanecarboxylic acid remained undepressed, whereas with the 2:4-dinitrophenylhydrazone of 2-oxo*cyclo*pentylacetic acid the mixed m.p. was depressed (180–187°).

The above acid was converted to its methyl ester by the methanol-sulphuric acid method, the infra-red spectrum of which showed that it was a mixture of methyl 3-oxo*cyclo*hexanecarboxylate and methyl 2-oxo*cyclo*pentylacetate, with the former predominating.

(*b*) A similar experiment using sodium (0·14 g.), ethanol (1·12 g.) and the diester (IV) (6·1 g.) was performed, except that the heating was continued for five days, when the triester (I) (2·9 g.) along with a keto-acid (0·1 g.) were obtained. The 2:4-dinitrophenylhydrazone of the latter was crystallised from dilute acetic acid, m.p. 213–215°. The m.p. remained undepressed with the 2:4-dinitrophenylhydrazone of 2-oxo*cyclo*pentylacetic acid, but was depressed with that of 3-oxo*cyclo*hexanecarboxylic acid.

Treatment of Diethyl β-Ethoxycarbonylpimelate (*I*) *with Sodium Ethoxide in Benzene.*—To dry sodium ethoxide, from sodium (0·6 g.), was added the triester (I) (7·2 g.) in dry benzene (20 ml.), and refluxed for 6 hr. The

β-keto-ester (3·1 g.), b.p. 120–130°/0·8 mm., isolated in the usual manner, was hydrolysed and decarboxylated with hydrochloric acid to yield a keto-acid, and this was identified as 3-oxo*cyclo*hexanecarboxylic acid by m.p. and mixed m.p. of the 2:4-dinitrophenylhydrazone.

Essentially the same experiment was repeated using two moles of sodium ethoxide. The methyl ester of the keto-monoacid was isolated in the usual way. The infra-red spectrum was identical with Fig. 4.

Reaction of Ethyl 1-Ethoxycarbonyl-2-oxocyclopentylacetate (IV) with Sodium Ethoxide in Benzene.—To dry sodium ethoxide, from sodium (1 g.), under dry benzene (8 ml.) was added the diester (IV) (9·5 g.), and heated for 8 hr. in an oil-bath at 130–140°. On working up in the usual manner, a product (6·7 g.) was collected at 125–127°/0·8 mm. This gives a deep purple colour with alcoholic ferric chloride. The product was dissolved in ether, and the β-keto-ester extracted with ice cold 5% alkali, and the alkaline extract acidified and worked up to yield a β-keto-ester (4·6 g.), b.p. 125–127°/0·8 mm. (Found: C, 60·07; H, 7·45%).

The β-keto-ester (3 g.) was hydrolysed by refluxing with hydrochloric acid (15%, 35 ml.), and the keto-monoacid (1·3 g.), thus obtained, was distilled at 110–120° (bath)/1 mm. The m.p. (202°) and mixed m.p. (201–202°) of its 2:4-dinitrophenylhydrazone showed it to be 3-oxo*cyclo*hexanecarboxylic acid.

SUMMARY

The isomerisation of ethyl 1-ethoxycarbonyl-2-oxo*cyclo*pentylacetate to ethyl 3-ethoxycarbonyl-2-oxo*cyclo*pentylacetate has been shown to proceed *via* diethyl β-ethoxycarbonylpimelate. The mechanism proposed by Chakravarti[1] is untenable. A mechanism based on the equilibrium nature of the reaction has been formulated to explain the formation of ethyl 3-oxo-*cyclo*hexane-1:2-dicarboxylate or ethyl 3-ethoxycarbonyl-2-oxo*cyclo*pentyl-acetate, as the major product, from diethyl β-ethoxycarbonylpimelate under different experimental conditions of Dieckmann cyclisation. Other mechanisms have also been discussed.

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