197. *Fused Carbon Rings. Introduction and Part I. The Fusion of Five-membered Rings in the* cis- *and* trans-*Positions. The Synthesis of β*-0 : 3 : 3-bicyclo*Octanones and Related Compounds.*

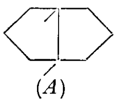
By R. P. Linstead and E. M. Meade.

Introduction.

Dicyclic compounds containing fused five-membered rings are of considerable stereochemical importance. This is best illustrated by a comparison with the corresponding cyclic type containing *cyclo*hexane units. Hückel has shown that two six-membered rings can be locked together in the ortho-position both by *cis*- and by *trans*-valencies in agreement with the Sachse–Mohr modification of the strain theory. Moreover, the *trans*-compounds so formed, in which the component rings must be multiplanar, are actually more stable than their *cis*-isomerides (Hückel, *Annalen*, 1925, **441**, 1; Windaus, Hückel, and Reverey, *Ber.*, 1923, **56**, 95).

If, on the other hand, there is any deviation from the plane in a *five-membered* ring (and more particularly in a *cyclo*pentane ring), the tetrahedral theory suggests that the molecule will become strained. From this the inference can be drawn either that a five-membered ring can only be fused to another ring in the *cis*-position or that if a *trans*-compound can be formed it will be unstable. A few simple compounds are known in which a *cyclo*pentane ring is fused to a *cyclo*hexane ring in the *trans*-ortho-position. Of these, *trans*-hexahydrophthalic anhydride (v. Baeyer, *Annalen*, 1890, **258**, 216) is unstable, as required by theory, but *trans*-β-hydrindanone is stable * and actually has a lower heat of combustion than the *cis*-isomeride (Hückel and Friedrich, *Annalen*, 1927, **451**, 132). This anomaly has led Hückel to the view that the strain theory cannot be applied in a simple manner to bicyclic systems (compare Mills, *Reports of the Fourth Solvay Conference*, 1931, p. 16).

It was considered that the 0 : 3 : 3-*bicyclo*octane system (*A* and *B*) would provide valuable evidence on this point. On the basis of the tetrahedral theory, the following properties could be predicted for this system :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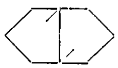
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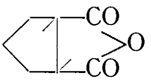

(*C*)

*cis-bicyclo*Octane derivatives (Type *A*) should have the stability of ordinary *cyclo*pentane compounds, but the *trans*-isomerides (Type *B*) should be comparatively unstable. In

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* To heat and reagents. No information is available on the relative stabilities of *cis*- and *trans*-α-hydrindanones in which free interconversion would be possible. The nomenclature here used is that of Hückel : hydrindane = hexahydrohydrindene ; hydrindanone = hexahydrohydrindone.

structures where conversion between the two types is possible, this should proceed in the direction *trans*- ⟶ *cis*-, that is, the reverse of that observed in decahydronaphthalenes. Hückel has also drawn attention to the importance attaching to these substances (" Theoretische Grundlagen der Organische Chemie," 1931, I, 63) * and has calculated that the *trans-bicyclo*octane ring has a strain nearly equal to that of (*cis*-)camphor.

The *bicyclo*octane system is also of considerable interest in relation to the structure of the bile acids and sterols (see p. 951).

*trans-bicyclo*Octane is associated stereochemically with the anhydride of *trans-cyclo*pentane-1 : 2-dicarboxylic acid (*C*) (E. Haworth and Perkin, J., 1894, **65**, 985). It is, however, doubtful whether this is a monomeric compound (compare Bredt, *Annalen*, 1924, **437**, 1; Hückel, *op. cit.*, p. 66; Goldsworthy and Perkin, J., 1914, **105**, 2639) and the substance will be re-investigated.

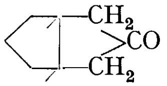
Investigation of the *bicyclo*octanes was commenced in 1930. Publication has been delayed to permit of confirmatory work on the orientation of the products, but has now been made advisable by the appearance of a paper by Ruzicka, de Almeida, and Brack (*Helv. Chim. Acta*, 1934, **17**, 183), which deals with compounds containing the same ring system. The main results reported in the present papers can be summarised as follows: In Part I it is shown that both *cis*- and *trans*-β-*bicyclo*octanones can be prepared, the former more readily. Part II describes the preparation of the corresponding α-ketone; in this case the *trans*-ketone cannot be isolated, as it is converted into the *cis*-isomeride by the action of heat or reagents. Part III deals with the *cyclo*pentane-1-carboxy-2-acetic acids related to the *cyclo*hexane-carboxy-acetic acids of Windaus, Hückel, and Reverey. It is shown that the anhydride of the *cis*-acid is more stable than that of the *trans*-acid, whereas the reverse is true of the *cyclo*hexane compounds.

These facts are in complete agreement with the requirements of the simple theory of ring strain based on the tetrahedral principle, and there is at present no indication of the operation of other factors in determining the stability of these bicyclic molecules. The pyrogenic formation of the multiplanar *trans*-β-ketone is no more surprising than that of camphor. It is hoped to institute soon a comparison between the heats of combustion of substances of the *cis*- and *trans*-series.

Part I.

When this work was commenced, no simple 0 : 3 : 3-*bicyclo*octanes of certain structure were known. Reference is made later to the products of Willstätter (*Ber.*, 1907, **40**, 957; 1908, **41**, 1480) and of Schroeter (*Annalen*, 1922, **426**, 1), which are of doubtful constitution.

For the synthesis of the *cis*- and *trans*-forms of β-0 : 3 : 3-bicyclo*octanone* (I and II) the corresponding cyclo*pentane*-1 : 2-*diacetic acids* (III and IV; R = H) were required.



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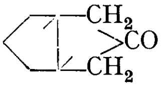

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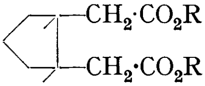

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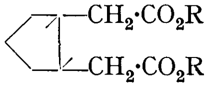

(IV.)

The only known acids of this type are the associated *cyclo*hexane-1 : 2-diacetic acids, but these have only been prepared by the oxidation of decalin derivatives or from aromatic compounds and no synthesis from simple mono-alicyclic compounds has previously been achieved.

Preliminary experiments were made (with the late Mr. J. F. F. Trotter of this College) on the condensation of 1 : 2-dibromo*cyclo*pentane with ethyl sodiomalonate in the hope that two side chains might be introduced either directly or (following Perkin) through the intermediate formation of a 0 : 1 : 3-*bicyclo*hexane derivative. No such reaction occurred owing to the ease with which hydrogen bromide was eliminated from the dibromide, and the method was not pursued. The bromine of ethyl 2-bromo*cyclo*pentanecarboxylate shows a similar lability.

The next possibility was to introduce a second side chain into a suitable substance

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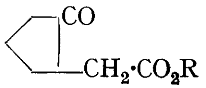
* This came to our notice two years after the first *bicyclo*octanone had been synthesised (1930).

already containing one acetic acid group such as ethyl *cyclo*pentanone-2-acetate (V; R = Et) or the lactone of *cyclo*pentanol-2-acetic acid (VI).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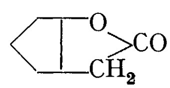
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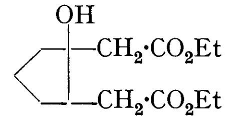
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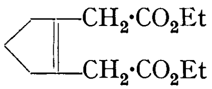
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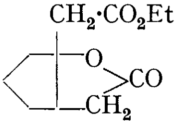
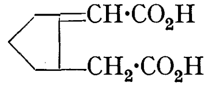

(IX.)

The ester (V), prepared by an improvement of Kotz's method from ethyl *cyclo*pentanone-carboxylate, gave on treatment with ethyl bromoacetate and zinc a poor yield of *ethyl* cyclo*pentanol*-1 : 2-*diacetate* (VII). A small amount of the same material was also given by the use of ethyl chloroacetate and magnesium, although Kon and Nargund report that *cyclo*pentanone itself does not yield a hydroxy-ester under these conditions (J., 1932, 2461). The hydroxy-acid corresponding to (VII) was obtained as a mixture of stereoisomerides and failed to yield a homogeneous acid on dehydration. The action of dehydrating agents on the ester (VII) yielded a mixture of ethyl *cyclo*pentene-1 : 2-diacetates (such as VIII) and the lactonic ester (IX), the latter in preponderating amount. This by-product was unfortunately of no synthetic value, as an attempt to reduce it to a saturated ester through the corresponding bromo-ester was unsuccessful.

The unsaturated ester was a mixture of Δ^{α}- and Δ^{β}-isomerides which on fractionation and hydrolysis gave two isomeric *acids*, $C_9H_{12}O_4$, m. p. 179° and 169—172°, the first of which is probably (X) and the latter a mixture of isomerides in which the position of the double bond is uncertain. The acid, m. p. 179°, was reduced catalytically to a mixture of saturated acids, from which cis-cyclo*pentane*-1 : 2-*diacetic acid* (III; R = H), m. p. 173°, could be isolated in small amount. The other unsaturated acid was reduced to an inseparable mixture of the isomeric diacetic acids. If the mixed unsaturated esters (such as VIII) were reduced, a mixture of saturated *cyclo*pentane-1 : 2-diacetic esters (III and IV; R = Et) was readily obtained which on hydrolysis yielded an inseparable mixture of acids. A process was subsequently developed whereby these mixtures could be used in the preparation of the pure dicyclic ketones. Care is necessary in dealing with the mixed diacetic acids, as they often crystallise in deceptively perfect forms. The melting points of such mixtures are, however, indefinite and alter on recrystallisation.

The next synthetic method tried was more successful. In the presence of piperidine or potassium ethoxide, ethyl *cyclo*pentanone-2-acetate condensed with ethyl cyanoacetate to yield *ethyl* cyclo*pentylidenecyanoacetate*-2-*acetate* (XII) in quantity. This was reduced by aluminium amalgam or catalytically to the corresponding saturated *ester* (XIII), which on hydrolysis gave *cis*-*cyclo*pentane-1 : 2-diacetic acid (III; R = H) contaminated with only a small amount of the *trans*-isomeride. This acid was identical with that prepared by the reduction of the unsaturated acid (X), m. p. 179°.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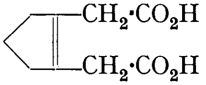
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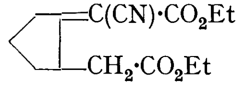
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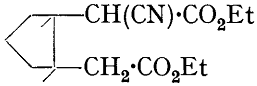
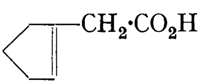

(XIII.)

A small amount of *cis*-β-*bicyclo*octanone (I) (the prefix 0 : 3 : 3- is omitted hereafter where there is no ambiguity) was formed during the hydrolysis of (XIII); which indicates the ease with which the *cis*-bicyclic system is formed.

Condensations of this type appear to be of general synthetic value for the preparation of *cis*-polycyclic systems. Another example will be found in Part II and the application of the method is being extended.

trans-*cyclo*Pentane-1 : 2-diacetic acid is relatively difficult to prepare. Its principal source has unexpectedly been the lactone (VI), which was expected to provide *cis*-material. This lactone has been prepared by the following five methods, of which the first is the most convenient. (i) The action of sulphuric acid on Δ^1-*cyclo*pentenylacetic acid (XIV); (ii) similarly from Δ^2-*cyclo*pentenylacetic acid (XV), prepared from *cyclo*pentadiene by Noller and Adams's method (*J. Amer. Chem. Soc.*, 1926, **48**, 2444); (iii) the action of sulphuric acid on *cyclo*pentanol-1-acetic ester (XVI); (iv) in small yield, by the action of acids on *cyclo*pentylidenecyanoacetic ester (XVII); and (v) the reduction of *cyclo*pentanone-2-acetic acid (V; R = H) with sodium amalgam or catalytically.



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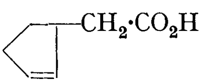

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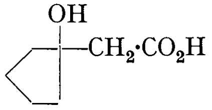

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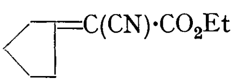
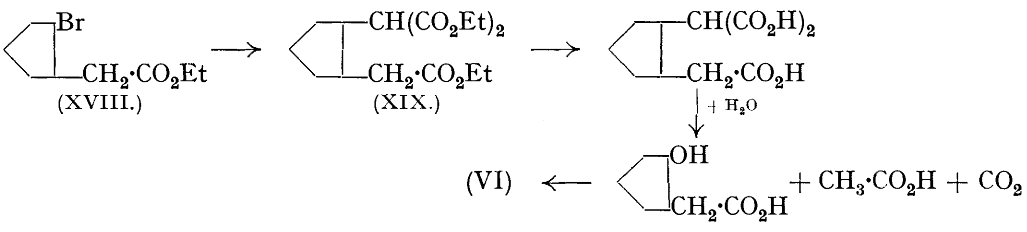


(XVII.)

It is possible for the lactone (VI) to exist in a *trans*- as well as a *cis*-form, although this is unlikely in view of the instability of the anhydride of *trans*-*cyclo*pentane-1 : 2-dicarboxylic acid. The products of all these reactions appeared from the concordance in physical properties to be the same homogeneous lactone, but, as it was liquid at − 70° and failed to yield a solid derivative with ammonia, aniline, phenylhydrazine, or hydrogen bromide, the presence of some of the *trans*-modification is not rigidly excluded. Nevertheless it behaved as a normal γ-lactone towards water and alkali, whereas the *trans*-lactone would be expected to yield the corresponding hydroxy-acid with unusual ease.

On treatment with phosphorus pentabromide and alcohol or with alcoholic hydrogen bromide the lactone yielded (? *cis* + *trans*)-2-*bromo*cyclo*pentaneacetic ester* (XVIII), a substance which slowly decomposed at room temperature into ethyl bromide, the parent lactone, and other products. Following Blanc's general methods for the synthesis of adipic acids, the reaction of this bromo-ester with ethyl sodiomalonate was next studied under a variety of conditions. The best yield of a product with the properties of *ethyl* cyclo*pentane*-1-*malonate*-2-*acetate* (XIX) was obtained by the use of molecular sodium and a large excess of ethyl malonate at 130°, but at low temperatures removal of hydrogen bromide occurred with the formation of Δ^1-*cyclo*pentenylacetic ester. The analytical figures of the condensation product, freed from ψ-acidic material, were approximately correct for the formula (XIX) but still rather low in hydrogen.

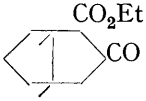
Hydrolysis of the malonic-acetic ester did not proceed smoothly either with acid or with alkali. trans-cyclo*Pentane*-1 : 2-*diacetic acid* (IV; R = H), m. p. 132°, was isolated in small and varying yield, together with acetic acid and the parent lactone (VI). The *trans*-acid was practically free from the *cis*-isomeride, and this fact, taken in conjunction with the re-formation of lactone, indicates that the acetic-malonic ester is a mixture in which only the *trans*-product is hydrolysed normally. The curious elimination of a side chain, apparently only from the *cis*-product, may proceed by the mechanism shown below. Some similar eliminations have been recorded but only from quaternary carbon atoms (Kenner, J., 1914, **105**, 2690; Beesley, Ingold, and Thorpe, J., 1915, **107**, 1087).



In any case the formation of *trans*-diacetic acid from what appears to be pure *cis*-lactone involves a change of configuration, which most probably occurs at the moment of the fission of the lactone ring during the formation of the bromo-ester. If unsaturated acid were temporarily formed during this reaction, the formation of *trans*-material would be not unexpected.

Formation of bicyclo*Octanes.*—When heated with a trace of baryta, the *cis*-acid was cyclised smoothly at 280° but the *trans*-acid only at 320°. The products were two isomeric ketones, $C_8H_{12}O$, both saturated and therefore dicyclic, but yielding two distinct *semicarbazones*, m. p. 197—198° and 251° respectively. These ketones are assigned the *cis*- (I) and the *trans*- (II) configuration respectively for reasons given later.

The ethyl ester of the *cis*-acid (III; R = Et) readily yielded *ethyl* cis-β-bicyclo*octanone-α-carboxylate* (XX) by the Dieckmann reaction. From its physical properties the ester existed mainly in the enolic form. On hydrolysis with alkali it regenerated the *cis*-acid, and with mineral acid yielded the *cis*-ketone (semicarbazone, m. p. 197—198°), both in a state of purity.



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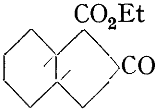
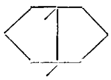


(XXI.)



(XXII.)

In the light of these results, the mixtures of diacetic acids inseparable by fractional crystallisation which had previously been obtained (p. 937) were re-examined. One such mixture was " fractionally ketonised " first below 315° and then at about 350°. From the first product the pure *cis*-semicarbazone was isolated, from the higher fraction the *trans*-. The mixed acids were also converted into the esters, which were treated with sodium in boiling benzene. Only the *cis*-ester formed a dicyclic keto-ester (XX) under these conditions: this yielded pure *cis-cyclo*pentane-1 : 2-diacetic acid on alkaline hydrolysis and pure *cis*-β-*bicyclo*octanone on acid hydrolysis, whilst the uncyclised ester was hydrolysed to the *trans*-diacetic acid. The *trans*-acid so obtained (m. p. 132°) was identical with that prepared from the lactone (VI), which provided a welcome confirmation of the structure. We believe this to be a unique example of a substituted adipic ester failing to undergo the Dieckmann reaction.

The reactions of the corresponding *trans-cyclo*hexane-1 : 2-diacetic acid present an instructive contrast. This acid when heated with baryta yielded a dicyclic ketone freely at 275° (Kandiah, J., 1931, 936, gives 260—270°; Thakur, J., 1932, 2152, gives 260—290°). Hückel and Friedrich (*loc. cit.*) have shown that its diethyl ester yields ethyl *trans*-β-hydrindanone-α-carboxylate (XXI) with boiling sodium ethoxide and we find that the same cyclisation occurs readily with sodium in boiling benzene, *i.e.*, under the conditions which fail to cyclise *trans*-1 : 2-*cyclo*pentanediacetic ester. This shows clearly the great difference in flexibility between the five- and the six-membered rings. The ease of ring-formations of this type depends upon the facility with which the carboxyl or carbethoxyl groups can come within reacting distance of one another, and hence not only on the normal positions of these groups but upon the flexibility of the ring structures which carry them.

cis-β-*bicyclo*Octanone was reduced to *cis*-0 : 3 : 3-*bicyclo*octane (XXII) by the Clemmensen and the Wolff method, the latter giving a rather purer product. The physical properties of this hydrocarbon (mean figures: b. p. 137°/760 mm.; $d_{4°}^{20°}$ 0·867; $n_{D}^{20°}$ 1·459, see p. 950) are of interest in comparison with those of certain previously investigated substances. Willstätter and Kametaka (*Ber.*, 1908, **41**, 1480) isolated a saturated bromide, $C_8H_{13}Br$, by the addition of hydrogen bromide to α-*cyclo*octadiene. This was converted into a mono-olefin, C_8H_{12}, and a saturated dicyclic hydrocarbon, C_8H_{14}, b. p. 140°, $d_{4°}^{20°}$ 0·8604, and $n_{D}^{20°}$ 1·4615. This was formulated as either 0 : 3 : 3-, 0 : 1 : 5-, or 0 : 2 : 4-*bicyclo*octane. The fair agreement between the physical properties supports the *bicyclo*-octane structure for this substance, but the comparative ease of reduction of Willstätter's hydrocarbon by nickel and hydrogen (*loc. cit.*) is not paralleled in the 0 : 3 : 3-*bicyclo*octane series and it is probable that the bridge is in one of the other positions.

The *bicyclo*octane of Vossen described by Schroeter (*loc. cit.*) was prepared by a method which affords no proof of structure. The high density of his hydrocarbon indicates that it could not have been a pure *bicyclo*octane; if it had had the *trans*-configuration, the density would have been lower than that of the *cis*-isomeride.*

It was next necessary to establish the configuration of the two forms of β-*bicyclo*-octanone by oxidation, which was expected to yield the *cis*- and the *trans*-form of cyclo-

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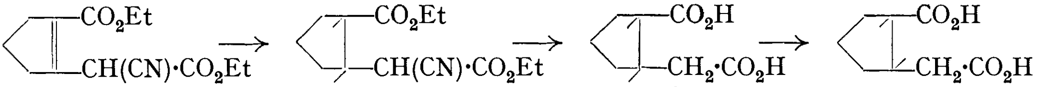
* Of other substances containing the *bicyclo*octane system, the acids of Wieland and the recent synthetic products of Ruzicka, which are both derivatives of α-*bicyclo*octanone, are discussed in Part II. Zelinski and Turowa-Pollak (*Ber.*, 1925, **58**, 1292) attribute the dimethyl*bicyclo*octane structure to the product of the isomerisation of decalin by aluminium bromide. This reaction has been reinvestigated with results to be reported shortly.

pentane-1-*carboxy*-2-*acetic acid* (XXIII and XXIV). These acids were easily synthesised for reference as follows: Ethyl *cyclo*pentane-1-carboxylate-2-cyanoacetate (XXV), prepared by catalytic reduction of the corresponding unsaturated ester (Kon and Nanji, J., 1932, 2426), was hydrolysed to a dicarboxylic acid, $C_8H_{12}O_4$, m. p. 89°. This on treatment with hydrochloric acid at 180° was converted into an isomeric acid, m. p. 66°. The latter is therefore given the *trans*- (XXIV), the former the *cis*- (XXIII), configuration. The further study of these acids is described in Part III.



(XXV.) (XXIII.) (XXIV.)

When *cis*-β-*bicyclo*octanone, regenerated from the semicarbazone, was oxidised with potassium permanganate in acetone, a good yield of *cis*-*cyclo*pentane-1-carboxy-2-acetic acid was obtained, the acid being identical with that prepared synthetically. The regenerated *trans*-ketone reacted more slowly under the same conditions to yield an oily product, which slowly deposited the same *cis*-acid in small quantity. A repetition of this experiment gave the same result. Such a change of configuration in the course of an oxidation is unusual but not unprecedented. Santene, which must contain two rings fused in the *cis*-positions, yields *trans*-*cyclo*pentanedicarboxylic acid on complete oxidation (Semmler and Bartelt, *Ber.*, 1908, **41**, 128, 381, 867) and *d*-Δ^3-carene (*cis*-) gives *l*-*trans*-caronic acid on oxidation with chromic acid (Gibson and Simonsen, J., 1929, 305). The results of oxidation cannot be taken as opposing the *trans*-configuration for the ketone of semicarbazone, m. p. 251°. Further experimental work on this point is in hand. The present evidence for the configuration of these and other *bicyclo*octanes is summarised in the next paper.

Among various abortive syntheses may be mentioned the following: the ethyl ester of (XXIII) failed to yield a *bicyclo*octanedionedicarboxylic ester by the action of oxalic ester under Komppa's conditions, neither did it give any appreciable amount of *bicyclo*octanedione on treatment with potassium in xylene (Kon, J., 1922, **121**, 513). *cyclo*Pentanone-2-carboxylic ester did not react with ethyl succinate in the manner suggested by Stobbe's condensation with *cyclo*pentanone itself.

EXPERIMENTAL.

1. *Preparations from Ethyl* cyclo*Pentanone-2-acetate.*—Ethyl *cyclo*pentanone-2-carboxylate, required in large quantities for this research, was prepared by the following improvement of the ordinary Dieckmann method. Ethyl adipate (606 g.) and molecular sodium (100 g., 50% excess) were boiled with 2·5 l. of benzene and 5 c.c. of absolute alcohol. Reaction commenced immediately and ended after 12 hours (steam-bath). The soft cake of the sodio-compound was decomposed with ice and dilute acid, and the keto-ester (402 g.) isolated, b. p. 102°/11 mm. (yield, 86%). The highest yield previously recorded is 70—80% (Dobson, Ferns, and Perkin, J., 1909, **95**, 2015). [The use of 100% excess of sodium raised the yield to 90%, but was disadvantageous, as some sodium was apt to be left unattacked. When twice the above quantities of ester and sodium were used in the same amount of benzene, the sodio-compound was inconveniently hard. The trace of alcohol eliminates the period of induction.]

Ethyl cyclo*pentanone-2-carboxylate-2-acetate.* Kötz (*Annalen*, 1906, **350**, 235) prepared this compound in 78% yield from ethyl sodio*cyclo*pentanonecarboxylate and ethyl bromoacetate in alcohol. We found it difficult to obtain steady yields by this process owing to ring fission to β-carbethoxypimelic ester, particularly when ethyl chloroacetate was used in place of the bromo-ester. Substitution of molecular sodium in benzene for sodium ethoxide gave repeatable yields of 75% of the required ester (peak yield, 85%) from either ethyl chloroacetate or bromoacetate. For instance, 69 g. of molecular sodium in 2·5 l. of benzene were refluxed with 468 g. of ethyl *cyclo*pentanonecarboxylate until no more hydrogen was evolved (2 hours); 404 g. of ethyl chloroacetate were then added and the mixture was heated (steam-bath) for some 90 minutes until an even suspension was obtained and then for a further 3 hours. The product was worked up in the usual manner, the crude ester, b. p. 150—180°/22 mm., being hydrolysed with 2 vols. of boiling concentrated hydrochloric acid. Hydrolysis was complete in 1 hour, and 5 hours more were required for decarboxylation. After removal of the mineral acid under reduced pressure, *cyclo*pentanone-2-acetic acid (V; R = H) distilled at 170—180°/5 mm. as an oil which soon solidified. Yield 87%, m. p. (crude) 52°; 53° after crystallisation from light petroleum (Kotz, *loc. cit.*, gives 50—51°).

The solid acid was esterified over-night at room temperature with 3 parts of alcohol saturated with hydrogen chloride, the ethyl ester being obtained in 90% yield, b. p. 123°/13 mm. The same product could be obtained from the crude undistilled acid, the yield then being 75—85% of the original dicarboxylic ester. The semicarbazone melted at 174°, in agreement with Kötz.

(*a*) *Cyanoacetic acid condensation.* Reaction between the ester and cyanoacetic ester in the presence of a little piperidine (3—4 days at room temperature, 1 hour on steam-bath) gave yields of 10—35% of condensation product, the remainder of the reagents being recovered quantitatively. The use of potassium ethoxide gave steady yields of 35%, but the recovery of reagents was not so good. The keto-ester (170 g.) was added at 0° with shaking to a suspension of potassiocyanoacetic ester from 113 g. of cyanoacetic ester and 39 g. of potassium in 500 c.c. of alcohol (calcium-dried). After a week at room temperature, the product was added to ice and an excess of dilute acid. The ester was taken up in ether and washed with sodium bicarbonate (essential). After removal of ether from the dried solution the residue was distilled; 30—40% of the initial materials were first recovered, followed by *ethyl* cyclo*pentylidenecyanoacetate-2-acetate* (XII), which distilled over the range 180—205°/5 mm. The b. p. was not much sharpened by redistillation and the product was presumably contaminated with isomeric material.* Yield 93 g., $d_{4^\circ}^{20^\circ}$ 1·111, $n_D^{20^\circ}$ 1·4883 (Found: C, 63·6; H, 7·4. $C_{14}H_{19}O_4N$ requires C, 63·4; H, 7·2%).

The ester was added to its own weight of amalgamated aluminium foil covered with moist ether, and the mixture left for 3 days after the end of the initial vigorous reaction. The product was filtered off, the alumina extracted with boiling ether, and the combined ethereal solutions washed with sodium bicarbonate solution, dried, and distilled. The product (70% yield) was still slightly unsaturated. Alternatively, the unsaturated ester in alcohol was shaken for 2 days with 2% of platinum oxide (Adams) in an atmosphere of hydrogen, absorption being theoretical. Unlike the parent unsaturated ester, *ethyl* cis-cyclo*pentane*-1-*cyanoacetate*-2-*acetate* (XIII) boiled constantly at 170—173°/5 mm. It had $d_{4^\circ}^{20^\circ}$ 1·0815, $n_D^{20^\circ}$ 1·4623, $[R_L]_D$ 67·91 (calc., 67·78), and was saturated to the usual reagents [Found (catalytic reduction): C, 63·0; H, 8·0; (aluminium amalgam reduction) C, 63·0; H, 7·8. $C_{14}H_{21}O_4N$ requires C, 62·9; H, 7·9%].

The reduced ester (83 g.) was boiled under reflux with concentrated hydrochloric acid (250 c.c.) for 10 hours and then distilled in steam. Ether extraction of the distillate yielded 3·1 g. (8%) of crude *cis*-β-*bicyclo*octanone, b. p. 75—80°/11 mm. (semicarbazone, m. p. 185—187°). The non-volatile portion was evaporated to dryness under reduced pressure, and the residue dissolved in sodium bicarbonate solution and extracted with ether. The acid, isolated from the bicarbonate solution by acidification and constant ether extraction, melted at 165° after draining on a tile (42·3 g., 73%), and at 173° after several crystallisations from water.

cis-cyclo*Pentane*-1 : 2-*diacetic acid* (III; R = H) is readily soluble in cold alcohol and hot water, moderately soluble in boiling benzene, and sparingly soluble in cold water or benzene. It crystallises in single needles from dilute solutions or wheatsheaf-like clusters from concentrated solutions and is saturated to permanganate and bromine [Found : C, 58·0, 58·2; H, 7·4, 7·6; equiv., 93·0, 92·9. $C_9H_{14}O_4$ requires C, 58·0; H, 7·6%; equiv. (dibasic), 93·1]. The *silver* salt is insoluble in water (Found : Ag, 53·9. $C_9H_{12}O_4Ag_2$ requires Ag, 54·0%).

(*b*) *Reformatski reaction.* The action of ethyl bromoacetate (or chloroacetate) and zinc (or magnesium) on ethyl *cyclo*pentanone-2-acetate was examined under the conditions summarised below. In all the experiments the product was washed with alkali before being freed from solvent and distilled. The yields given are those of ester, b. p. 170°/20 mm.—180°/5 mm. The quantities employed were : 57 g. of keto-ester, 62 g. of ethyl bromoacetate (10% excess), 35 g. of zinc (50% excess), and 100 c.c. of dry solvent, except in experiment 6, where a 50% excess of bromo-ester and 100% excess of zinc were employed, and in experiment 7.

Expt.	Solvent.	Conditions.	Yield.
1	Xylene	1 Hour at b.p. after vigorous reaction	6 g., 7%
2	Toluene	,, ,, ,, ,,	10·4 g., 12%
3	Benzene	,, ,, ,, ,,	13·0 g., 15%
4	Toluene	10 Mins. ,, ,, ,,	15·6 g., 18%
5	Benzene	,, ,, ,, ,,	19·9 g., 23%
6	Benzene	,, ,, ,, ,,	23·2 g., 27%
7	Benzene and equivalent amounts of Mg and $CH_2Cl·CO_2Et$		11·3 g., 13%

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* The reaction with piperidine as condensing agent has since been improved by Mr. J. Barrett, and the ester obtained as a solid.

After redistillation, ethyl cyclo*pentanol*-1 : 2-*diacetate* (VII) boiled at 143—144°/4 mm.; $d_{4^\circ}^{20^\circ}$ 1·1170, $n_D^{20^\circ}$ 1·4678, $[R_L]_D$ 64·22 (calc., 64·87) (Found : C, 60·7, 60·9; H, 8·3, 8·5. $C_{13}H_{22}O_5$ requires C, 60·5; H, 8·6%). The alkali-soluble material isolated by acidification (140 g.) gave on esterification mainly a product, b. p. 215—220°/3 mm.

Ethyl *cyclo*pentanol-1 : 2-diacetate was dehydrated with phosphoric oxide or, better, by Darzens' method. The ester (41 g.) in 27·5 c.c. of pyridine and 100 c.c. of dry ether was treated below 5° with 12 c.c. of thionyl chloride. After 2 hours at room temperature the product yielded (*a*) 5·8 g., b. p. 120—130°/3 mm., (*b*) 3·8 g., b. p. 130—140°/3 mm., and (*c*) 22·5 g., b. p. 140—160°/3 mm. By fractional distillation of (*a*) and (*b*) the following two products were isolated, both of which were mixtures of unsaturated esters, $C_{13}H_{20}O_4$:

	B.p./3 mm.	$d_{4^\circ}^{20^\circ}$.	$n_D^{20^\circ}$.	$[R_L]_D$ (calc. 61·14).
(1)	126—128°	1·0815	1·4876	61·68
(2)	134—137	1·0795	1·4680	61·84

[Found : (fraction 1) C, 64·7; H, 8·1; (fraction 2) C, 64·8; H, 8·2. $C_{13}H_{20}O_4$ requires C, 65·0; H, 8·2%].

From fraction (*c*) there was isolated a liquid, b. p. 166°/6 mm., $d_{4^\circ}^{20^\circ}$ 1·1430, $n_D^{20^\circ}$ 1·4737, which reacted only slowly with bromine or permanganate, could not be reduced catalytically, and was soluble in cold dilute alkali solution. It was probably the *lactone* of cyclo*pentanol*-1-*acetic ester*-2-*acetic acid* (IX) (Found : C, 61·7; H, 7·7. $C_{11}H_{16}O_4$ requires C, 62·3; H, 7·6%. $[R_L]_D$ found, 52·1; calc., 51·8).

The unsaturated ester fractions (1) and (2) were hydrolysed separately with alcoholic potash. The acid from (1), m. p. 155—160° (crude), formed small granular crystals, m. p. 169—172° (slight decomp.), from water and was obviously a mixture of isomeric unsaturated acids (Found : C, 58·8; H, 6·5. $C_9H_{12}O_4$ requires C, 58·7; H, 6·6%). The acid from (2) gave a solid acid contaminated with oil. The drained solid melted at 160° (crude) and after a few crystallisations from water yielded cyclo*pentylideneacetic acid*-2-*acetic acid* (X), m. p. 179° (sharp, no decomp.) (Found : C, 58·6, 58·4; H, 6·5, 6·4. $C_9H_{12}O_4$ requires C, 58·7; H, 6·6%).

2 G. of the acid of m. p. 179° were reduced (alcohol, Adams's PtO_2), hydrogen being rapidly absorbed up to the theoretical amount for one double bond. The saturated acid first separated as prisms, m. p. 162°, and after 5 crystallisations melted at 173° alone or mixed with *cis-cyclo*pentane-1 : 2-diacetic acid prepared by the cyanoacetic ester process. The acid obtained by reduction of the unsaturated acid of m. p. 169—172° was exhaustively crystallised, but no pure diacetic acid could be separated from it.

Another sample of the unsaturated ester obtained by dehydration of the Reformatski product was reduced catalytically to ethyl *cis*- and *trans-cyclo*pentane-1 : 2-diacetates, b. p. 122°/3 mm., $n_D^{20^\circ}$ 1·4514 (the pure *cis*-ester has $n_D^{20^\circ}$ 1·4521) (Found : C, 64·7; H, 9·3. Calc. : C, 64·4; H, 9·2%). The acid obtained on hydrolysis yield no pure diacetic acid on careful crystallisation (but see p. 945).

2. *Preparation from the Lactone of* cyclo*Pentanol-2-acetic Acid* (VI).—*Syntheses of the lactone.* (*a*) *In quantity by the Reformatski reaction.* For the preparation of *cyclo*pentanone from adipic acid, " Organic Syntheses," V, 37, recommends the use of mechanical stirring for quantities exceeding 200 g. This is unnecessary; pyrolysis of 1·5 kg. of the acid (3 l. flask, without stirring at 295—300°) has given yields (84%) larger than that reported. The yield of *pure cyclo*pentanol-1-acetic ester from the ketone by the Reformatski reaction was never greater than 33%. The reactants (up to 4 g.-mols.) could be kept under control by working in a 5 l. flask with wide double-surface condensers. 621 G. of the hydroxy-ester, 725 c.c. of pyridine, and 1·5 l. of dry ether were dehydrated at 0° during 2 hours (mechanical stirring) with 280 c.c. of thionyl chloride. After a further 2 hours, 461 g. of crude Δ^1-*cyclo*penteneacetic ester were isolated (81·5%), which was hydrolysed to the acid (XIV) (compare Kon and Linstead, J., 1925, **127**, 616; Kon and Nargund, J., 1932, 2461). The crude acid was lactonised with 4 vols. of 60% (vol.) sulphuric acid for 20 minutes at 90°. The cold product was poured on ice, saturated with ammonium sulphate, and extracted with ether (Linstead, J., 1932, 115). The lactone boiled constantly at 124°/17 mm.; yield 78%, *i.e.*, 64% of the hydroxy-ester. The lactone could also be made directly from the hydroxy-ester by treatment with boiling dilute sulphuric acid, but the yields were less satisfactory (35—50%).

(*b*) Ethyl *cyclo*pentylidenecyanoacetate (Harding and Haworth, J., 1910, **97**, 489) gave a poor yield of lactone on treatment with hydrochloric acid or with a mixture of sulphuric and acetic acids at the boiling point.

(*c*) *From* cyclo*pentadiene.* 25 G. of the diene were converted by Noller and Adams's method (*loc. cit.*) through Δ^2-*cyclo*pentenylmalonic acid, m. p. 148°, into 10·7 g. of Δ^2-*cyclo*pentenylacetic acid, b. p. 107—110°/13 mm. On treatment with 4 vols. of 60% sulphuric acid (by vol.) at 90° for 20 minutes, this yielded 5·8 g. of lactone, b. p. 120—121°/12 mm.

(*d*) *From* cyclo*pentanone-2-acetic acid.* 71 G. of the keto-acid (p. 940) in 250 c.c. of water and 20 g. of caustic soda were reduced with 1·5 kg. of 5% sodium amalgam, added in ten approximately equal portions during 5 days, the mixture being kept faintly acid with hydrochloric acid. After a further week's standing, the solution was acidified and boiled, and the lactone extracted with ether and freed from acids with sodium bicarbonate. Yield 18 g. (28%), b. p. 115—116°/10 mm. A little unchanged keto-acid was recovered, but the bulk of the acid product was polymeric. A small amount of lactone was also obtained by catalytic reduction (platinum) of the keto-acid in ethereal solution, but the reaction was very slow (compare Schuette and Thomas, *J. Amer. Chem. Soc.*, 1930, **52**, 3010).

Catalytic reduction of the ester of the keto-acid was attempted without success (i) in alcohol, ether, and acetic acid at atmospheric temperature and pressure, and (ii) at 110° and 2·5 atmospheres, with amyl alcohol and also without solvent. When the keto-ester was treated with sodium and dry alcohol, and the product acidified with dry hydrogen chloride, only polymeric products were obtained.

The *lactone* of cyclo*pentanol-2-acetic acid* (VI) was obtained by these methods as a colourless mobile oil with a lactonic odour; it was appreciably soluble in water, completely soluble in caustic soda, and boiled constantly at 130°/20 mm. or 98°/4 mm. (Found: C, 66·3, 66·5; H, 8·1, 8·1. $C_7H_{10}O_2$ requires C, 66·6; H, 8·0%). It contained no free acid; the equivalent by back-titration was 128·2 (calc., 126·1). The physical properties of the various preparations are given below :

Method	*a.*	*b.*	*c.*	*d.*
$d_{4^\circ}^{20^\circ}$	1·116	—	1·118	—
$n_D^{20^\circ}$	1·473	1·475	1·472	1·472

From (*a*), $[R_L]_D$ = 31·70 (calc., 31·58).

Preparation of trans-cyclo*pentane*-1 : 2-*diacetic acid.* The lactone (126 g.) was added to phosphorus pentabromide from 135 c.c. of the tribromide (excess) and 55 c.c. of bromine. The mixture was warmed (steam-bath, shaking) until a vigorous reaction set in and then for a further 30 minutes. The product was poured into 200 c.c. of alcohol, cooled, and shaken with ice and water. The aqueous layer was separated from the heavy oil and extracted with ethyl bromide; the extract was added to the oil, and the whole washed with excess of ice-cold aqueous caustic potash. This removed unreacted lactone but did not affect the bromo-ester. After recovery of the ethyl bromide the residual oil was carefully fractionated to separate the monobromo-ester (139 g., b. p. 128—132°/20 mm.; 60%) from some (?) dibrominated material (b. p. 130°/7 mm., 10 g.).

An ice-cold solution of the lactone (31·5 g.) in absolute alcohol (100 c.c.) was saturated with hydrogen bromide (*ca.* 200 g.). After 15 hours at 0° the product was poured into water and worked up exactly as in the process described above. In both processes more ethyl bromide was recovered than had been used to extract the aqueous layers. The yield of bromo-ester was 43 g. (73%), b. p. 125°/15 mm., and there was no high fraction. *Ethyl 2-bromo*cyclo*pentane-acetate* (? *cis* and *trans*) has a very persistent, sweet smell [Found: (PBr_5 method) Br, 34·2; (HBr method) Br, 34·0. $C_9H_{15}O_2Br$ requires Br, 34·0%]. It decomposes slowly at room temperature, readily at the boiling point under atmospheric pressure, into the parent lactone, ethyl *cyclo*pentenylacetate, ethyl bromide, and hydrogen bromide.

The condensation of the bromo-ester and ethyl sodiomalonate was examined with the results summarised below. The products were worked up as usual; the low fractions contained malonic and Δ^1-*cyclo*pentenylacetic esters, but no bromo-ester unless the condensation was carried out at 20°. The yields stated are those of crude high-boiling ester, b. p. 160°/15 mm.—210°/5 mm. (M = malonic ester, B = bromo-ester).

(1) 2·3 G. of sodium in 100 c.c. of absolute alcohol treated with 16 g. of M and then with 23·5 g. of B; 10 hours at b. p. Yield 5·4 g., 17%. (2) 2·3 G. of molecular sodium treated with 4·6 g. of dry alcohol in dry ether, 16 g. of M added, and then 23·5 g. of B in 100 c.c. of xylene; after the ether had been boiled off, the mixture was refluxed for 6 hours; yield 6·9 g., 22%. (3) As (2), but the sodiomalonate was made in xylene from molecular sodium; yield 9·5 g.,

30%. (4) As (3), but 2 mols. of M being used; yield 13·5 g., 43%. (5) As (3), but 4 mols. of M being used; yield 14·8 g., 47%. (6) As (5) at room temperature for a week; no high-boiling product was found and the bromo-ester was recovered quantitatively. (7) As (6), potassium being used, the result being the same. (8) Poorer yields were also obtained by the use of benzene in place of xylene.

Redistillation of the various products separately gave a main fraction, b. p. 174°/5 mm., for which the following analyses were obtained :

Preparation No.	4.	5.	8.
% C	62·0	61·7	60·9, 61·2
% H	7·3	7·3	7·1, 7·2

($C_{16}H_{26}O_6$ requires C, 61·1; H, 8·3%). When the ester from (5) was shaken with 10% potash solution, *ethyl* cyclo*pentane*-1-*acetate*-2-*malonate*, still not quite pure, was recovered. Found : C, 61·5; H, 7·5%. [These figures are very near those required for an unsaturated ester ($C_{16}H_{24}O_6$ requires C, 61·5; H, 7·8%), a formulation which would agree with the ease with which the side chain is eliminated but not with the method of formation.] The potash solution yielded 3% of a ψ-acidic *product*, m. p. 94°, leaflets from benzene–petroleum [Found (micro) : C, 52·6, 52·4; H, 5·9, 5·6%]. This compound was free from halogen, gave a brown colour with ferric chloride, and decolorised bromine : its constitution is unknown.

The acetic-malonic ester was boiled with concentrated hydrochloric acid (10 vols.) for 6 hours, the acid being allowed to distil over slowly (A). The residual solution was filtered from tarry matter and evaporated to dryness; a poor yield of diacetic acid remained, m. p. 130° after being drained, 132° after several crystallisations. It was sometimes necessary to complete the decarboxylation by heating the crude hydrolysis product at 180° for a few minutes. trans-cyclo*Pentane*-1 : 2-*diacetic acid* (IV; R = H) forms clusters of short transparent prisms from water or dilute alcohol, cubes from benzene. It is sparingly soluble in water and hydrocarbons, and stable to bromine and permanganate [Found : C, 57·9, 57·8; H, 7·4, 7·6; equiv., 92·6, 93·3, 93·5. $C_9H_{14}O_4$ requires C, 58·0; H, 7·6%; equiv. (dibasic), 93·1]. On one occasion a sample of an acid, m. p. 137°, was obtained. This may be the true m. p., but no subsequent preparation has been obtained melting above 132° after many crystallisations. No second acid could be isolated.

The distillate obtained during the hydrolysis (at A above) was redistilled; the first runnings yielded no semicarbazone. The residue was separated in the usual manner into acidic and ψ-acidic fractions. The acid fraction contained acetic acid (*p*-bromophenacyl ester, m. p. and mixed m. p. 85°). The ψ-acidic fraction yielded the original lactone of *cyclo*pentanol-2-acetic acid, b. p. 130°/20 mm., $n_D^{20°}$ 1·475.

The yield of the *trans*-diacetic acid was variable but always low, the best being 2·0 g. of acid from 12 g. of acetic-malonic ester, but frequently practically none could be isolated. We have been unable to trace the reason for this variation.

3. *Formation of* bicyclo*Octane Derivatives*.—(i) cis-*Ketone from* cis-*acid*. A mixture of *cis*-*cyclo*pentane-1 : 2-diacetic acid (21·2 g., m. p. 169—170°) and 0·15 g. of baryta was gently heated in an open beaker up to 225°, and the molten mass poured into a 50 c.c. flask (mechanical loss due to bulky apparatus was thus diminished). The mixture was heated (air-bath) to 270°, the ketone then being first evolved. Reaction proceeded smoothly at 280° and was completed at 310°. The distillate was washed with alkali and fractionated, 9·6 g. (70%) of ketone passing over at 78°/10 mm. This was converted into semicarbazone (almost theoretical yield), which was systematically crystallised from alcohol; a small amount of a higher-melting, less soluble semicarbazone having been eliminated, the pure *semicarbazone* of cis-β-bicyclo*octanone* was obtained as beautiful, transparent, prismatic needles, m. p. 197—198° (Found : C, 59·2, 59·4; H, 8·4, 8·5; N, 23·2. $C_9H_{15}ON_3$ requires C, 59·6; H, 8·3; N, 23·3%). On distillation with an excess of aqueous oxalic acid, this regenerated cis-β-bicyclo*octanone* (I) in almost theoretical yield; b. p. 78°/10 mm., $d_{4°}^{19°}$ 1·0084, $n_D^{19°}$ 1·4799, $[R_L]_D$ 34·96 (calc., 34·76) (Found : C, 77·1; H, 9·8. $C_8H_{12}O$ requires C, 77·4; H, 9·8%). The substance has a pleasant ketonic odour and is saturated to the usual reagents.

(ii) cis-*Ketone from* cis-*ester*. The *cis*-diacetic acid (3·3 g., m. p. 172°) was converted *via* the silver salt into the *diethyl* ester (III; R = Et) (3·2 g.), b. p. 160°/17 mm., $d_{4°}^{18°}$ 1·0323, $n_D^{18°}$ 1·4521, $[R_L]_D$ 63·28 (calc., 63·34) (Found : C, 64·3; H, 9·1. $C_{13}H_{22}O_4$ requires C, 64·4; H, 9·2%). 2·70 G. of this were boiled over-night with 0·45 g. of molecular sodium in 25 c.c. of dry benzene. The product was cooled, poured on ice, and extracted with 5% caustic potash solution. The unchanged ester in the benzene layer was hydrolysed to the pure *cis*-acid, m. p. 171—172°. The alkaline solution was acidified and extracted with ether; the extract was washed with sodium bicarbonate solution, dried, and distilled; 1·32 g. of *ethyl* cis-bicyclo*octan-2-one-*1-*carboxylate* (XX) were thus obtained over the range 134—138°/17 mm. (b. p. 136°/17 mm.). The ester smelled like ethyl *cyclo*pentanone-2-carboxylate, gave an intense dark blue colour with ferric chloride, and had $d_{4°}^{19°}$ 1·0791, $n_D^{19°}$ 1·4845, whence $[R_L]_D$ 52·01 (calc. for keto-form 50·26, for enol-form, 51·31) (Found : C, 67·1; H, 8·2. $C_{11}H_{16}O_3$ requires C, 67·3; H, 8·2%).

0·6 G. of the keto-ester was hydrolysed with 20 c.c. of boiling concentrated hydrochloric acid for 3 hours, 15 c.c. of liquid being allowed to distil over. This yielded 0·26 g. (45%) of *cis*-β-*bicyclo*octanonesemicarbazone, m. p. (crude) 196°, (recryst.) 197—198°. Another equal quantity of keto-ester was hydrolysed similarly with 0·5 g. of caustic potash in 10 c.c. of water. The products were the *cis*-ketone (semicarbazone, m. p. 197—198°) and *cis*-*cyclo*pentanediacetic acid, m. p. 173° alone or mixed with an authentic sample.

(iii) trans-*Ketone from* trans-*acid.* 2·4 G. of *trans*-*cyclo*pentane-1 : 2-diacetic acid (m. p 130—131°) were heated with 0·1 g. of baryta. The ketone, which was freely evolved at about 340°, was isolated in the same manner as the *cis*-isomeride (0·7 g., b. p. 190°/756 mm.). A similar experiment with 0·71 g. of the *trans*-acid, m. p. 137°, yielded 0·22 g. of ketone, b. p. 74°/18 mm. The *semicarbazone* of trans-β-bicyclo*octanone* (II) was readily formed in almost quantitative yield. It was sparingly soluble in boiling alcohol and also much less soluble in benzene than the *cis*-isomeride. The crude semicarbazone, m. p. 238°, was boiled with successive small quantities of alcohol, the m. p. rising to a steady value of 251°. The substance then crystallised from dilute acetic acid or boiling absolute alcohol in clusters of small needles [Found (micro) : C, 59·8; H, 8·5; N, 23·4. $C_9H_{15}ON_3$ requires C, 59·6; H, 8·3; N, 23·3%]. The ketone was regenerated from the semicarbazone as a colourless oil with a coarser odour than that of the *cis*-ketone.

(iv) *Fractional ketonisation of mixed acids.* 2·9 G. of mixed *cis*- and *trans*-diacetic acids (p. 942) were heated with 0·2 g. of baryta first at 270—290° and then at 310° for 30 minutes. The ketone evolved (0·38 g., 20%) gave a semicarbazone, m. p. 192—196°. The temperature was then raised; reaction recommenced at 325° and was completed at 370°. 0·33 G. of ketone isolated from the second distillate gave a semicarbazone, m. p. 245° after two washings with a little boiling alcohol. After crystallisation from dilute acetic acid and another washing with boiling alcohol the product had m. p. 250° and did not depress the m. p. of the *trans*-semicarbazone.

(v) *Selective ring closure of mixed esters.* 3·3 G. of mixed *cis*- and *trans*-*cyclo*pentane-1 : 2-diacetic esters (p. 942) were boiled over-night with 0·4 g of molecular sodium in 25 c.c. of benzene. The product was separated, as described under (ii) above, into a keto-ester and uncyclised dibasic ester. The keto-ester was hydrolysed by alkali into *cis*-β-*bicyclo*octanone (semicarbazone, m. p. and mixed m. p. 196—197°) and *cis*-*cyclo*pentane-1 : 2-diacetic acid (m. p. and mixed m. p. 171—172°). The uncyclised ester was hydrolysed to *trans*-*cyclo*pentane-1 : 2-diacetic acid (m. p. and mixed m. p. 131—132°).

4. *Reactions of* β-bicyclo*octanones.* (*a*) Reduction of the *cis*-β-ketone. The Clemmensen reduction was conveniently carried out in an all-glass apparatus comprising a flask fitted with a wide side-tube inclined at 45°. A gas-delivery tube fitted with a safety bulb was led by means of a ground-glass joint through the main neck to the bottom of the flask. The side-neck was fitted by a ground-glass joint to a condenser bent at right angles so that it could be used either for reflux, or, by swivelling the joint, for downward distillation. The ketone was added to a mixture of amalgamated zinc, hydrochloric acid, and acetic acid in the flask, and hydrogen chloride was passed in from time to time through the delivery tube. In this apparatus *trans*-β-decalone yielded 75% of pure *trans*-decalin ($d_{4°}^{20°}$ 0·8718) and a little *trans*-β-decalol.

5·7 G. of *cis*-β-*bicyclo*octanone were reduced with 70 g. of amalgamated zinc, 50 c.c. of glacial acetic acid, and 25 c.c. of concentrated hydrochloric acid. The mixture was refluxed gently with occasional passage of hydrogen chloride and after 8 hours the condenser was turned round and the hydrocarbon distilled over. A trace of ketone was removed with bisulphite and the hydrocarbon was refluxed over sodium and distilled over fresh sodium.

The following modified Wolff reduction was kindly carried out by Mr. A. H. Cook.

cis-β-*bicyclo*Octanonesemicarbazone (m. p. 194—195°, 3·2 g.) was heated with a solution of 1·5 g. of sodium in 15 c.c. of alcohol and 0·5 g. of palladised barium sulphate. The alcohol was distilled off, and the residue heated at 200° for 2½ hours. The distillate was extracted with light petroleum, washed with dilute acid, dried, and distilled. Yield, 1·2 g. (60%) of colourless hydrocarbon, b. p. 137—138°, which was redistilled over sodium.

cis-0 : 3 : 3-bicyclo*Octane* had a dull but characteristic smell and was saturated to the usual reagents. The physical properties of the two samples (compare p. 950) were :

Method.	B.p./mm.	$d_{4°}^{t°}$.	n_D.	t.	$[R_L]_D$.
Clemmensen	136°/761	0·8687	1·4649	20°	35·04
Wolff	137·5/748	0·8702	1·4609	16·2	34·71

[Found : (Clemmensen product) C, 87·0; H, 13·0. C_8H_{14} requires C, 87·2; H, 12·8%].

(*b*) Regenerated *cis-β-bicyclo*octanone (1·90 g.) was added to a solution of potassium permanganate (4·85 g.) in 250 c.c. of water and 50 c.c. of acetone. The mixture was shaken mechanically for 36 hours, the acetone removed in steam, and the residue acidified, cleared with sulphur dioxide, and exhaustively extracted with ether. The extract was shaken with sodium bicarbonate solution, and the acid recovered (1·20 g., solidifying rapidly). After being pressed on a tile, it was crystallised by passing hydrogen chloride into its aqueous solution. The acid melted at 89° alone and at 90—91° when mixed with *cis-cyclo*pentane-1-carboxy-2-acetic acid (below).

(*c*) 0·33 G. of the pure semicarbazone of *trans-β-bicyclo*octanone (m. p. 251°) was distilled with oxalic acid and the first 25 c.c. of distillate were treated with 25 c.c. of acetone and 0·55 g. of potassium permanganate in 25 c.c. of water. After 3 days' shaking, the product was worked up as under (*b*) above to yield a colourless gum. After this had been kept for a long time in a vacuum desiccator, a small amount of a solid acid separated, m. p. 75—79° alone and 84—87° in admixture with *cis-cyclo*pentane-1-carboxy-2-acetic acid. The oxidation of the *cis*-β-ketone was repeated on the same small scale and readily yielded the pure *cis*-acid similar to that isolated in (*b*).

5. *Synthesis of* cis- *and* trans-cyclo*Pentane*-1-*carboxy*-2-*acetic Acids.*—Ethyl 2-carbethoxy-Δ^1-*cyclo*pentenylcyanoacetate (Kon and Nanji, *loc. cit.*) was completely hydrogenated in 2 days (2% Adams's PtO_2 catalyst, in alcohol). The yield of the reduced ester (XXV) of b. p. 158—163°/5 mm. was 90%. This was boiled for 4 hours with 4 vols. of concentrated hydrochloric acid, and the solution filtered and evaporated to dryness under reduced pressure. The acid was dissolved in ether and extracted with sodium bicarbonate solution, from which it was recovered as a gum which solidified. The solid was dissolved in a little water and saturated with hydrogen chloride, which liberated crystals, m. p. 87—89°. After a repetition of the process the pure *cis*-acid (XXIII) was obtained, m. p. 89° (Found : equiv., 86·3, 86·1. Calc., 86·0. For other analytical figures, see p. 961). 2 G. of this acid were heated at 180° (sealed tube) with 6 c.c. of concentrated hydrochloric acid for 8 hours. The solution was filtered and extracted with ether. The *trans*-acid (XXIV) so isolated (1·49 g.) could not be crystallised from hydrochloric acid but formed clusters of thin needles, m. p. 68°, from light petroleum (see p. 960). The *silver* salt separated in needles (Found : Ag, 55·8. $C_8H_{10}O_4Ag_2$ requires Ag, 56·0%).

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