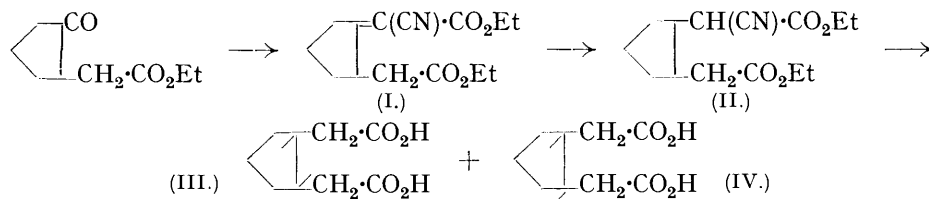


95. Fused Carbon Rings. Part IV. Further Investigation of 0:3:3-bicycloOctanones in Relation to the Strain Theory.

By J. W. BARRETT and R. P. LINSTEAD.

THE investigation of *cis*- and *trans*-bicyclooctane derivatives already described (Linstead and Meade, J., 1934, 935; Cook and Linstead, *ibid.*, p. 946) was incomplete in three respects: (1) owing to preparative difficulties, sufficient material of the *trans*-series could not be accumulated for an examination of the physical properties; (2) no absolute proof of configuration was obtained; (3) the structure of *trans*- β -bicyclooctanone was not substantiated by oxidation. The completion of this work is now described.*

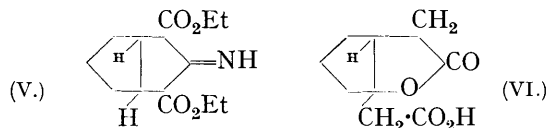
trans-cyclopentane-1:2-diacetic acid (III) has been prepared in quantity by an improvement of the process of Linstead and Meade (*loc. cit.*):



The essential feature is that the mixture of *cis*- and *trans*-acids (IV and III) obtained by the hydrolysis of (II) can be completely freed from the *cis*-isomeride by ketonisation with baryta at 280–300°, and the residual *trans*-acid isolated from the residue in a yield of over 20%.

The melting point of this key-substance was in some doubt. We had previously found values of 132° and 137°, and Hückel and his collaborators obtained preparations melting between 135° and 140°. The purity of this material is essential for the preparation of homogeneous *trans*-bicyclooctane derivatives and for resolutions. It is now found that the pure acid melts at 133° and that higher-melting products contain the *cis*-isomeride as impurity. The melting point of the *trans*-acid is raised by admixture with the *cis*-isomeride.

The direct formation of *cis*- β -bicyclooctanone in small amount during the hydrolysis of (II) was confirmed. A simple explanation is that preformed dicyclic material is present as impurity in (II), for example, the isomeric imine (V) (compare Best and Thorpe, J., 1909, 95, 685).



The method by which (V) is formed is obscure. Ring-closure of (II) during the reduction seems unlikely. The alternative explanation is that some unsaturated dicyclic material

* Since our first publication Hückel, Goth, and Demmler (*Ber.*, 1934, 67, 2102) and Hückel and Goth (*ibid.*, p. 2104) have described the independent synthesis in small amount of the same intermediate compounds. The methods used were similar to ours and the results are in general agreement. A novel point is that they obtained some *cis*-cyclopentane-1:2-diacetic acid by the oxidation of 5-hydrindanol. This helps to confirm the general stereochemical relationships of these compounds.

is present in (I). Against this is the fact that such a substance would contain a double bond adjacent to the bridge-head and would be strained. Experiments with a view to the isolation of these possible dicyclic intermediates were fruitless.

The preparation of *trans*-cyclopentane-1:2-diacetic acid from the lactone of cyclopentanol-2-acetic acid (Linstead and Meade, *loc. cit.*) was confirmed, but the method is definitely inferior to that mentioned above. This lactone has been more fully investigated by Hückel and Gelmroth (*Annalen*, 1934, 514, 233). Acid hydrolysis of the unsaturated cyano-ester (I) yielded the *lactonic acid* (VI), but this could not be reduced to a saturated dibasic acid.

cis- and *trans*-cyclopentane-1:2-diacetic acids are respectively *meso*- and racemic compounds. Hence a resolution of the acid of m. p. 133° would provide absolute evidence of its *trans*-configuration. The acid has been resolved by means of its brucine salt, and a *levo*-acid, m. p. 151°, $[\alpha]_{D}^{20} - 63.5^\circ$, isolated. This and related compounds which are still under investigation will be described in a later paper.

dl-trans-cyclopentane-1:2-diacetic acid gave a 50% yield of *trans*- β -bicyclooctanone when heated with baryta at 340°. Blanc's process gave a poorer yield of the same product. Hückel, Goth, and Demmler (*loc. cit.*) obtained only a trace of ketone by Blanc ring closure of a crude *trans*-acid of melting point 139–140°. In Table I our yields are compared with those obtained from the *cis*-acid under similar conditions.

TABLE I.

Yields, %, of bicycloOctane Derivatives from cyclopentane-1:2-diacetic Acids and Esters.

Method.	<i>cis</i> -.	<i>trans</i> -.
Baryta	72 at 280° (+6%) *	50 at 340° (+11%)*
Blanc	61 (+1%)	24 (+ nil)
Dieckmann	44	nil

* Figures in parentheses indicate the recovery of uncyclised acid.

The poor yield in such cyclisations, particularly by the Blanc and the Dieckmann reaction, when there is some resistance to the approach of the carboxyl or carbethoxyl groups, has also been noticed among adipic acids derived from sterols by oxidation (compare Wieland and Dane, *Z. physiol. Chem.*, 1932, 210, 271; Stange, *ibid.*, 1933, 218, 74; Vocke, *Annalen*, 1933, 508, 1).

trans- β -bicycloOctanone (regenerated from its carefully purified semicarbazone) was oxidised by both nitric acid and potassium permanganate to *trans*-cyclopentane-1-carboxy-2-acetic acid in good yield,* the product being identical with synthetic material (Cook and Linstead, *loc. cit.*). The structure of the ketone is therefore established. Reduction of its semicarbazone by the Kishner–Wolff method yielded *trans*-bicyclooctane. Owing to the large amount of *cis*- β -bicyclooctanone obtained as a by-product in the preparation of *trans*-cyclopentanediacetic acid, it was possible thoroughly to purify this ketone and the derived *cis*-bicyclooctane for determinations of physical constants. The *trans*-ketone was also obtained pure, but *trans*-bicyclooctane has so far been obtained only in small amount.

TABLE II.

Physical Constants of bicycloOctane Derivatives.

	<i>cis</i> -bicycloOctane.	<i>trans</i> -bicycloOctane.	<i>cis</i> - β -bicycloOctanone.	<i>trans</i> - β -bicycloOctanone.
B. p./mm.	136°/755	132°/755	78°/10, 195°/755	62°/10, 189°/755
M. p. (corr.) (liquid at -70°)		-36°	-33° to -34°	+13° to +14°
d_4^{18}	0.8718	0.8626	1.0102	0.9963
n_D^{18}	1.4629	1.4625	1.4811	1.4791
$[R_L]_D$	34.74	35.12	34.97	35.34
Exaltation	+0.01	+0.37	+0.21	+0.58

* Previous oxidations (Linstead and Meade, *loc. cit.*) had yielded an oil which deposited a trace of solid *cis*-cyclopentane-1-carboxy-2-acetic acid. A considerable quantity of the pure *trans*-ketone has, however, now been oxidised by each of us to the *trans*-acid. The early anomaly was probably due to the facts that the *cis*-ketone had not been completely eliminated and that the *cis*-acid formed by its oxidation crystallised first owing to its higher melting point and lower solubility.

The *cis*-compounds are higher-boiling and lower-melting than their *trans*-isomerides. A similar difference was observed by Hückel in the case of the isomeric decalins and decalones. The older values for the *cis*-compounds (Cook and Linstead, J., 1934, 950) are in good agreement with those quoted above. The Auwers-Skita rule (*Annalen*, 1919, 420, 92) is obeyed. The difference in the molecular refractivity between pairs of *cis*- and *trans*-bicycloisomerides is remarkably constant (the *trans*- always having the higher value), thus: decalins, 0·38; α -decalones, 0·37; β -decalones, 0·32; bicyclooctanes, 0·38; β -bicyclooctanones, 0·36.

The heats of combustion of the two ketones and of the *cis*-hydrocarbon were kindly carried out by Prof. Dr. W. A. Roth and Dr. G. Becker of Braunschweig, to whom we are greatly indebted.

Heats of Combustion

(weights not corrected to vacuum).

	Cals. per g. at 20° (mean of 4).	Kg.-cals per mol.	
		Constant volume.	Constant pressure.
<i>cis</i> -bicycloOctane.....	10,785 \pm 3	1187·4	1189·4
<i>cis</i> - β -bicycloOctanone	8,816 \pm 3	1094·1	1095·6
<i>trans</i> - β -bicycloOctanone	8,871 \pm 2	1100·9	1102·4

Bearing on the Strain Theory.—These results conclusively establish the fact that two five-membered rings can be linked by *trans*- as well as by *cis*-valencies and justify a fuller theoretical treatment than was made in the introduction to Part I.

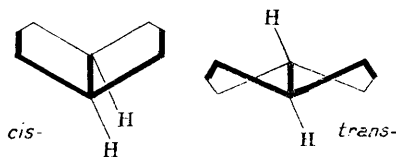
It is generally recognised that the discovery by Ruzicka of stable large carbon rings necessitates the revision of the original Baeyer strain theory. Hückel's investigations of dicyclic ring systems provided strong evidence for the correctness of a purely tetrahedral theory of ring strain (Sachse-Mohr). According to this, rings in which the carbon atoms are tetrahedrally disposed contain the least energy and are stable, and deviations from this state lead to instability. The evidence is not, however, completely explicable on this basis. Both *cis*- and *trans*-forms of the decalin ring may be presumed to contain a tetrahedral disposition of the carbon atoms, yet Hückel has shown that the *cis*-ring is comparatively unstable, for *cis*- α -decalone yields the *trans*-isomeride readily and apparently irreversibly, and Roth and Lassé find that the heats of combustion of *cis*-decalin and *cis*- β -decalone are higher than those of their *trans*-isomerides (*Annalen*, 1925, 441, 48). Even more unexpected are the results from the hydrindane series, for which the tetrahedral theory requires a strainless *cis*- and a strained *trans*-arrangement.* Here again the heats of combustion give anomalous results (Hückel and Friedrich, *Annalen*, 1927, 451, 132; Hückel, "Theoretische Grundlagen der Org. Chemie," 1934, p. 63). On the other hand, the available evidence suggests that *cis*- α -hydrindanone is more stable than the *trans*-isomeride (Windaus, Hückel, and Reverey, *Ber.*, 1923, 56, 95), and experiments in these laboratories by Dr. A. H. Cook point in the same direction but are inconclusive.

These conflicting facts have led to the suggestion that the stability of dicyclic rings—

* It is necessary to draw attention to two errors in a recent paper by Tudor and Vogel (J., 1934, 1250). After describing the accepted stereochemical arrangement of the *trans*-hydrindane molecule, these authors say "A possible but less probable alternative for the *trans*-system is a planar 5-ring and a planar (and therefore strained) 6-ring (see Hückel, *Fortschr.*, 1927, 19, Heft 4, 31)." It is self-evident that it is impossible to join any two planar rings by *trans*-valencies and the "alternative" is therefore incorrect. The stereochemistry of the system is correctly discussed by Hückel in the reference cited. Tudor and Vogel conclude from their experiments that "there is some real difference [between the *trans*-decalin and the *trans*-hydrindane system]. . . . This conclusion . . . differs from that of Thorpe (J., 1931, 1023), who regards both ring systems as strainless. A possible interpretation of this difference is that the methods employed [by Thorpe's school] . . . are not sufficiently sensitive to detect the small differences present." The actual conclusion drawn by Thorpe in the reference cited reads as follows: "We are therefore faced with the fact that when the six-membered ring is locked in this way all strain ceases or is so far diminished as to be incapable of detection by the methods we have applied." The "possible interpretation" of Tudor and Vogel has thus already been made and their comment is a misrepresentation.

and hence by implication of simple rings—may be affected to a greater extent than has been previously thought by factors other than strain, in particular the repulsive forces of the constituent atoms (Hückel, *Fortschr. Chem. Physik phys. Chem.*, 1927, **19**, 1; Mills, *Rep. Inst. Solvay*, 1931, 17). If it is admitted that this may be a major factor, we can no longer be sure that the well-known instability of rings containing fewer than 5 carbon atoms is due primarily to their divergence from a tetrahedral arrangement.

The isomeric bicyclooctanes yield decisive evidence on this point. The *cis*-form contains two inclined planar cyclopentane rings and is strainless; the *trans*-system contains two multiplanar cyclopentane rings, and there is considerable divergence from the tetra-



hedral arrangement. On the other hand, the interatomic repulsions will be *less* in the *trans*- than in the *cis*-compound. Hence, as Hückel says, "The investigation of this system can bring about a decision of the suitability of the regular tetrahedron. If it were shown that here the *trans*-form was poorer in energy than the *cis*-, the conception of the regular tetrahedron would have to be abandoned" (*op. cit.*, p. 67).

The methods by which the stability of isomeric cyclic compounds can be compared are : (a) From the differences between their heats of combustion. The assumption is made that for practical purposes this is parallel to the difference between their free energies; this is probably justified for compounds of similar physical characteristics. (b) Less rigidly, by measurements of the equilibrium between interconvertible isomerides, and by comparison between the ease of formation and the ease of fission of the two ring systems.

The ease of fission of *cis*- and *trans*-bicyclooctanes has not been compared, but the other methods show that the *trans*-system is richer in energy and less stable than the *cis*-. Thus, *trans*- α -bicyclooctanone is converted into the stable *cis*-isomeride under the conditions of formation (Cook and Linstead, *loc. cit.*); the greater ease of formation of the *cis*- β -over *trans*- β -bicyclooctanone is illustrated in Table I; and the difference between the heats of combustion of the isomeric β -bicyclooctanones (6.8 kg.-cals.) is exceptionally large, and the *trans*-ketone is at the higher level of energy.

The comparative instability of the *trans*-bicyclooctane ring therefore provides a rigid proof of the reality of strain in the sense of a resistance of the tetrahedral carbon atom to distortion. There seems no evidence from this series alone of the operation of any other factor affecting ring-stability, but when the chemistry of ortho-dicyclic systems is considered as a whole, the possibility has to be admitted that, when the strain is small, the stability of the ring may be affected by minor factors.

If the heat of combustion of *cis*-bicyclooctane (1187.4) is compared with that of *cis*-decalin (1499.9),* the difference for each CH_2 is found to be normal (156.2). The corresponding difference between *cis*- β -decalone and *cis*- β -bicyclooctanone is also about normal (155.1 for each CH_2). Hückel has calculated on a tetrahedral basis that the strain in the *trans*-bicyclooctane molecule is nearly equal to that of camphor. The difference between the heat of combustion of camphor and that of *trans*- β -decalone, which is a strain-free isomeride, is 10.6 kg.-cals. (Roth's values). A more direct comparison, because between two liquids of similar boiling point, may be made between the isomeric fenchane and *trans*-decalin. The former, which has the same strain as camphor, has a heat of combustion of 1502.1 (Zubov-Swientoslavski); the latter, which is strain-free, a value of 1494.8 (Roth-Hückel). The difference, 7.3 kg.-cals., is very close to that (6.8) now found by Roth and Becker between the isomeric β -bicyclooctanones, between which on the tetrahedral theory there should be the same difference in energy.

* This and the other older values are taken from the compilation by Roth in Landolt-Börnstein "Tabellen" (1923, I, 1591; 1927, 331) and represent kg.-cals. per mol. at constant volume.

EXPERIMENTAL.

Preparation of trans-cyclopentane-1:2-diacetic Acid and of cis- and trans-β-bicycloOctanones.—Ethyl cyclopentanone-2-acetate was prepared by Linstead and Meade's method. Light petroleum (b. p. 60—80°) is a more convenient solvent than benzene for the preparation of the intermediate ethyl cyclopentanone-2-carboxylate-2-acetate. With a view to improving the poor yield previously obtained in the condensation of this keto-ester with cyanoacetic ester, the condensation of cyclopentanone and cyanoacetic ester in the presence of piperidine was first systematically investigated; the tabulated figures indicate the yields of solid ethyl cyclopentylidencyanoacetate obtained from 5 g. of cyclopentanone and 6.8 g. of cyanoacetic ester in the times stated:

Hours at room temp.	$\frac{1}{2}$	1	2	4	—	—	—	—	$\frac{1}{2}$	1	3	4
Hours at 100°	—	—	—	—	$\frac{1}{2}$	1	2	4	$\frac{1}{2}$	$\frac{1}{2}$	1	$\frac{1}{2}$
Yield, g.*	—	0.1	0.1	0.9	0.6	1.9	2.8	4.7	2.4	2.6	4.3	4.9
Yield, g.†	4.9	5.8	6.2	7.9	6.1	6.8	6.9	7.9	7.0	7.6	7.8	8.0

Catalyst: piperidine, *0.25 g., †1 g.

An increase in the concentration of cyanoacetic ester did not quicken the reaction. The rate of condensation obviously depends upon the concentration of piperidine, and a maximum yield of about 75% is obtainable. An increase in piperidine concentration had a good effect also on the much slower reaction between cyclopentanone-2-acetic ester and cyanoacetic ester. 900 G. of the keto-ester, 600 g. of cyanoacetic ester, and 25 g. of piperidine were left for 14 days in a stoppered bottle. On distillation the mixture yielded 55% of unchanged esters (b. p. 90—125°/12 mm.), which were left to condense with a further quantity of piperidine, and 41% of the condensation product (I). After two distillations the latter boiled completely at 177°/2 mm.—172°/1 mm. and partly solidified. The solid formed clusters of small prisms, m. p. 58°, from light petroleum. The unsolidified portion boiled at 172—174°/2 mm. Both were unsaturated to the usual reagents [Found: (solid) C, 63.6; H, 7.1; (liquid) C, 63.6; H, 7.3. Calc. for (I): C, 63.4; H, 7.2%]. The liquid presumably contains some isomeride differing in the position of the double bond. The original ester of Linstead and Meade (which was mainly prepared by the use of potassium ethoxide as catalyst) had a wider boiling range, yielded no solid, and was more readily reduced by hydrogen over platinum.

The solid ester (I) was hydrolysed with 3 vols. of boiling hydrochloric acid for 36 hours. The product was evaporated to dryness under reduced pressure, extracted with sodium bicarbonate solution, acidified, and isolated by means of ether. The oil obtained solidified on standing and yielded massive octahedra, m. p. 83°, from benzene-petroleum. A similar hydrolysis of the crude ester (I) gave the same product, which was a saturated lactonic acid and appeared to be the lactone of cyclopentanol-1:2-diacetic acid (VI) (Found: C, 58.5; H, 6.5; acid equiv., 184.4; lactone equiv., 183. C₉H₁₂O₄ requires C, 58.7; H, 6.6%; equiv., 184). It gave no definite compound on reduction with zinc and acid, sodium amalgam, or phosphorus and hydriodic acid.

Reduction of (I) (compare Linstead and Meade, *loc. cit.*). Only in a few isolated cases could any catalytic reduction be obtained over Adams's platinum catalyst. Hydrogenation over palladium on barium sulphate or Raney's catalyst also proved abortive. Aluminium amalgam gave consistent yields of 75% on a fairly large scale. The saturated ester (II) boiled at 172°/2 mm. (Found: C, 63.1; H, 7.8. Calc.: C, 62.9; H, 7.9%).

Hydrolysis of (II). 200 G. of the saturated ester were refluxed with 500 c.c. of concentrated hydrochloric acid for 12 hours, and steam-distilled. *cis-bicycloOctanone* (b. p. 78°/10 mm.; semicarbazone, m. p. 197—198°) was isolated from the distillate in 4% yield in the manner already described (*loc. cit.*). The residue from the steam distillation deposited 110 g. (79%) of mixed cyclopentane-1:2-diacetic acids, and ether extraction of the filtrate yielded practically nothing more. The acids melted crude at 149—155° and at 155—156° after one crystallisation from water (Found: equiv., 93.0. Calc., 93.05). Twelve fractional crystallisations from water yielded the pure *cis*-acid, m. p. 172—173°, as the least soluble product; the most soluble fraction melted at 137—138° but was not pure *trans*-acid (see below). Fractional crystallisation of various salts gave no useful separation, although the disodium salt of the *cis*-acid was relatively sparingly soluble in water and gave some pure *cis*-acid.

Separation and Ring Closure of Diacetic Acids.—(1) The separation by the Dieckmann method previously reported was confirmed, but the overall yield was not good. The diethyl ester from 20 g. of mixed acids, m. p. 155—156°, ultimately yielded 4.1 g. of *cis-bicyclooctanone*

(44%) and 0.75 g. (5%) of *trans*-acid, m. p. 132°. The following is the best process for the separation of the *trans*-acid.

(2) A mixture of 60 g. of the acid of m. p. 155—156° with 5 g. of baryta was heated in a bath of mixed nitrates at 280°; the *cis*-ketone distilled regularly. When the evolution of ketone slackened, the temperature was kept at 300° for 2 hours. The black residue was extracted twice with boiling, very dilute hydrochloric acid, which deposited the *trans*-acid, m. p. 131°. After one crystallisation from benzene and one from water, *trans*-cyclopentane-1:2-diacetic acid was obtained pure as massive transparent cubes, which effloresced on exposure to air (Found: C, 58.0; H, 7.6; equiv., 93.0. Calc.: C, 58.0; H, 7.6%; equiv., 93.05). The *cis*- β -bicyclooctanone formed during this reaction was isolated by means of a little petrol (b. p. 40—60°) and washed with sodium bicarbonate solution and water. After being dried and freed from solvent, it boiled at 78°/15 mm., and gave a semicarbazone, m. p. 198° after one crystallisation. The bicarbonate extract yielded a small quantity of mixed acids (m. p. 152—154°). Yield: 13 g. (20%) of *trans*-acid and 22 g. (55%) of *cis*-ketone.

The pure *trans*-acid melts sharply at 133°, and no higher-melting acid has been obtained in a number of these cyclisations. When the acid is heated at 280—300° with baryta for some time, it gives no ketone and is recovered almost quantitatively and unchanged in melting point. On the other hand, 11.2 g. of acid of m. p. 137—138° (obtained by exhaustive crystallisation of the mixed acids) on similar treatment gave 7.5 g. of the *trans*-acid (m. p. 132—133°) and 2.1 g. of the semicarbazone of *cis*- β -bicyclooctanone (m. p. 197—198°). The material of m. p. 137—138° is thus a mixture of about 70% of *trans*- and 30% of *cis*-acid. Intimate mixtures of the two acids in known quantities melted sharply at the temperatures given below:

% <i>trans</i> -Acid	0	10	25	50	66.6	75	80	95	100
M. p.	173°	167.5°	159.5°	147.5°	140°	136.5°	135°	133.5°	133°

(3) When treated with baryta in exactly the same way, the pure *cis*-acid (m. p. 172—173°) gave 72% of *cis*-ketone, and 6% of the *cis*-acid was recovered (compare Linstead and Meade, *loc. cit.*). 10 G. of the *cis*-acid were heated slowly to 230—240° with 25 c.c. of acetic anhydride. When the distillation slackened, the temperature was kept at 260° for 30 minutes. The ketone isolated in 61% yield was the pure *cis*-isomeride (semicarbazone, m. p. 197—198°), and 1% of the *cis*-acid (m. p. 172°) was recovered.

(4) A mixture of 20.2 g. of the *trans*-acid (m. p. 132—133°) and 1.5 g. of baryta was heated by a mixed nitrate bath to 320° (internal temperature) without evolution of ketone. Reaction commenced between 320° and 330°, ketone was evolved freely at 340°, and the process was complete at 350° after 2 hours. *trans*- β -bicyclooctanone, isolated in the usual way, boiled at 61—62°/10 mm. (yield, 50%) and gave the insoluble semicarbazone already described by Linstead and Meade, m. p. 243—245° (crude). 10.1 G. of this were just dissolved by 2.5 l. of boiling methyl alcohol, and the solution deposited 9.9 g. of the pure semicarbazone in massive transparent rhombs, often aggregated in star-like clusters, m. p. 249° (decomp.). The melting point depends upon the rate of heating; the above values were obtained with samples put in a bath at 240°. In spite of the prolonged heating in this cyclisation, as much as 2.25 g. (11%) of *trans*-cyclopentanediacetic acid were recovered, m. p. 132—133°.

Purification of the β -bicyclooctanones. The yields of pure semicarbazones obtained from the distilled ketones are remarkably high. The *cis*-ketone gives 95.3% of the semicarbazone, m. p. 197—198°, and the *trans*-ketone 98% of that of m. p. 249°. The *cis*-ketone was regenerated in the usual way and was extracted with purified light petroleum. The solution was washed with sodium bicarbonate solution and water and dried over sodium sulphate. The ketone was distilled from a Claisen flask to which a long side-arm carrying a short condenser was fused, so that the vapour did not come into contact with corks (Found: C, 77.3; H, 9.8%). *trans*- β -0:3-bicyclooctanone was regenerated and purified similarly (Found: C, 77.3; H, 9.8. C₈H₁₂O requires C, 77.4; H, 9.8%). For determination of the physical constants (Table II) the ketones were distilled in a vacuum in an all-glass apparatus and the data were determined on small middle fractions, although each ketone distilled constantly.

Oxidation of the trans-ketone. (1) The regenerated ketone (0.5 g.) was added during 15 minutes to 4 c.c. of concentrated nitric acid at 90—100° under reflux. The mixture was heated for a further 15 minutes and then left over caustic potash in a vacuum desiccator. The semi-solid mass was shaken with sodium bicarbonate solution and ether. The bicarbonate extract was then acidified and extracted with ether. The residue from the ether was an oil which rapidly solidified in a vacuum desiccator. It was extracted with three successive quantities of 50 c.c. of boiling petroleum (40—60°). Each extract deposited the same product, m. p. 60°, and

there was scarcely any residue undissolved after the third extraction. The material of m. p. 60°, twice crystallised from petroleum (b. p. 40—60°), formed small white needles, m. p. 64°, and 64—65° on addition of the synthetic *trans*-cyclopentane-1-carboxy-2-acetic acid (m. p. 66°) of Cook and Linstead (*loc. cit.*) (Found : C, 55·7; H, 6·9. Calc. : C, 55·8; H, 7·0%).

(2) The regenerated ketone (0·5 g.) in 12 c.c. of acetone was added to 1·28 g. of potassium permanganate dissolved in 60 c.c. of water. The mixture was shaken in a stoppered bottle for 48 hours, the acetone removed in steam, and the solution acidified, cleared with sulphur dioxide, and extracted with ether. The acid in the extract was purified through sodium bicarbonate and by extraction with boiling light petroleum in exactly the same way as was that from the nitric acid oxidation. It melted at 63—64° and did not depress the melting point of the latter product or of the synthetic acid.

cis-bicyclo*Octane*.—A mixture of 18·5 g. of the pure *cis*-semicarbazone (m. p. 197—198°), 17 g. of powdered caustic potash, and a little methyl alcohol (to aid mixing) was heated with a free flame. After removal of the alcohol the bicyclooctane distilled at 190—220° (internal temperature). After 2 hours' heating, the distillate was taken up in a little ether, washed with dilute acid, solutions of sodium bisulphite and bicarbonate, and finally with water. After being dried over calcium chloride, the solvent was removed through a short column, and the residue distilled. The fraction (10·6 g.), b. p. 137—139°, from two such runs was refluxed for $\frac{1}{2}$ hour over sodium and then redistilled twice, the physical properties of the fraction (8·0 g.) of b. p. 137°/755 mm. being taken. It was then distilled over potassium and redistilled (7·6 g.), b. p. 136°/755 mm. The physical properties (Table II) were identical with those observed before the distillation with potassium. For the determination of the heat of combustion a sample was redistilled from an all-glass apparatus and sealed.

trans-bicyclo*Octane*.—3 G. of the *trans*-semicarbazone, m. p. 249°, were evaporated to dryness with 1 g. of sodium and sufficient dry alcohol. The product was heated at 200—220° for $\frac{1}{2}$ hour, the hydrocarbon which distilled being collected and purified in the manner described above. 0·74 G. of a fraction, b. p. 131—132°/755 mm., was refluxed over sodium for $\frac{1}{2}$ hour, distilled from sodium, and redistilled; 0·68 g. of 0 : 3 : 3-*trans*-bicyclooctane was isolated, b. p. 132°/755 mm., which was used for the measurement of the physical constants (Table II) (Found : C, 87·5; H, 12·8. C₈H₁₄ requires C, 87·2; H, 12·8%).

A solid *by-product*, isolated from the crude hydrocarbon, crystallised from dilute alcohol in long transparent prisms, m. p. 188°. It was soluble in the usual organic solvents, insoluble in water, saturated to permanganate, left no residue on ignition, and contained no nitrogen (Found : C, 78·6; H, 10·1%). Its composition is unknown.

Experiments with the (cis-) Lactone of cyclopentanol-2-acetic Acid (compare Linstead and Meade, *loc. cit.*; Hüchel and Gelmroth, *loc. cit.*).—25 G. of Δ^1 -cyclopentenylacetic acid were heated with 125 c.c. of 50% sulphuric acid on the steam-bath for 20 minutes, 20 g. of lactone, b. p. 125°/16 mm., being obtained (1). An exactly similar result was obtained when a mixture of Δ^1 -cyclopentenylacetic acid and cyclopentylideneacetic acid was used (2). Both samples boiled constantly and had the correct equivalents {Found : (1) C, 66·5; H, 8·0; [R_L]_D, 31·62; (2) C, 66·5; H, 8·1; [R_L]_D, 31·64. Calc. : C, 66·6; H, 8·0%; [R_L]_D, 31·58}.

Each sample was converted into the hydroxy-acid, and the velocity of lactonisation of this determined in the usual manner (J., 1932, 128). The two samples gave identical results (50% lactonisation in 8 minutes, 90% in 60 minutes). The curve obtained by plotting the percentage of lactonisation against time showed no inflexion. The equilibrium between hydroxy-acid and lactone in water was determined separately (Boorman and Linstead, J., 1933, 580) and was at 95·8% of lactone for each sample. The results are those expected for a normal γ -lactone carrying β - and γ -substituents and it is concluded that the lactone is the strain-free *cis*-isomeride.

The lactone was converted into ethyl cyclopentane-1-acetate-2-malonate, which again did not give quite the correct analysis (compare Linstead and Meade, *loc. cit.*). 30 G. of this ester yielded 1·0 g. of *trans*-cyclopentane-1 : 2-diacetic acid on hydrolysis with concentrated hydrochloric acid, together with acetic acid and the original lactone. The acid had m. p. and mixed m. p. 132° (Found : C, 57·9; H, 7·6; equiv., 93·1. Calc. : C, 58·0; H, 7·6%; equiv., 93·05).

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