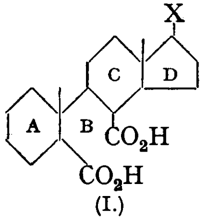
181. *Fused Carbon Rings. Part XVII. The Stereoisomerism of the Perhydrodiphenic Acids and an Examination of the Blanc Rule.*

By R. P. LINSTEAD and A. L. WALPOLE.

The perhydrodiphenic acids are important for two reasons : (i) They are related stereochemically to the perhydrophenanthrenes and can be used for the determination of their configuration. (ii) They can be used for testing the limitations of the Blanc rule, dealing with the formation of cyclic ketones from dibasic acids, and for correlating the ease of ketonisation with the configuration.

Six inactive perhydrodiphenic acids are theoretically possible, and four of these are described in the present paper. Previous work by Vocke and by Hückel is reviewed and the configurations of the various acids are discussed. All the acids yield anhydrides and three give cyclic ketones.

BLANC's rule (*Compt. rend.*, 1907, **144**, 1356) formed one of the main principles in the determination of the size of the carbocyclic rings present in sterols and similar substances. Expressed briefly, it states that if two carboxyl groups occupy the 1 : 3-, 1 : 4-, or 1 : 5-positions in a chain, the acid on treatment with acetic anhydride and subsequent distillation will yield an anhydride, whereas 1 : 6- and higher dicarboxylic acids (with certain limitations) will give cyclic ketones. The rule, although usually applicable, fails in certain cases for reasons not fully understood.

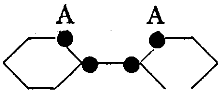


(I.)
(X = Bile-acid side chain.)

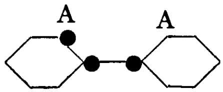
A notable exception is thilobilianic acid, with the skeleton structure (I), which yields only an anhydride on pyrolysis (Wieland and Dane, *Z. physiol. Chem.*, 1932, **210**, 268). Wieland and Dane suggested that 1 : 6-dicarboxylic acids did not obey the Blanc rule when the two carboxyl groups were attached to two rings not fused together. Ruzicka (*Helv. Chim. Acta*, **1933**, **16**, 216, 327) pointed out that the breakdown of the rule might have a stereochemical origin, for both in thilobilianic acid and in the other exceptional acids (Windaus, *Z. physiol. Chem.*, 1933, **213**, 155; Wieland and Weyland, *ibid.*, 1920, **110**, 141) there is a *trans*-linking between B and C. Hence, unless an inversion of configuration occurred, the pyro-ketone formed would contain a five-membered ring fused to two six-membered rings by at least one *trans*-fusion. Ruzicka suggested that the exceptions to the Blanc rule are confined to this type.

In 1934, Vocke obtained important evidence bearing on the problem from a study of synthetic compounds. By the hydrogenation of diphenic ester over nickel, and subsequent hydrolysis, he prepared two perhydrodiphenic acids, m. p. 213° and 245°, together with incompletely reduced material (*Annalen*, 1934, **508**, 1). Both these acids yielded anhydrides on treatment with acetic anhydride, but not on pyrolysis. The higher melted and gave a ketone on pyrolysis; the lower sublimed unchanged. In a short addendum to Vocke's paper, Hückel describes the preparation of a third perhydrodiphenic acid, m. p. 273°, by the catalytic hydrogenation of diphenic acid over platinum. The new acid yielded a ketone by the Blanc procedure.

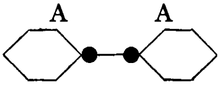
In the present work we have prepared four stereoisomeric perhydrodiphenic acids, studied their behaviour on pyrolysis, and made some progress in the determination of their configurations. The stereochemistry of the acids resembles that of the perhydrophenanthrenes. There are four possible racemic and two *meso*-modifications, which may be formulated as (II) to (VII). The possibility of restricted rotation about the link joining the two rings is neglected for the purpose of the present discussion.



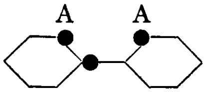
(II.) *meso.*



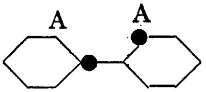
(III.) rac.



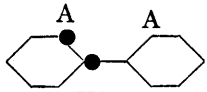
(IV.) *meso.*



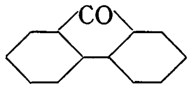
(V.) rac.



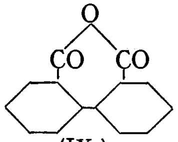
(VI.) rac.



(VII.) rac.



(VIII.)



(IX.)

(The convention is the same as before, A being CO_2H.)

The acids were prepared as follows. The oxidation of 9-ketoperhydrophenanthrene, m. p. 51° (preceding paper), with nitric acid failed to yield a solid product, but a similar oxidation of the corresponding alcohol, made by the Ponndorf–Verley method, yielded a *perhydrodiphenic acid*, m. p. 202—203°. The isomeric 9-ketoperhydrophenanthrene, m. p. 49°, was readily oxidised to a perhydrodiphenic acid, m. p. 244°, together with traces of a more degraded product. The acid was recovered unchanged after treatment with a mixture of hydrochloric and acetic acids at 200°. The catalytic hydrogenation of diphenic acid in glacial acetic acid over Adams's catalyst slowly yielded a perhydro-acid, m. p. 273—274°, clearly identical with that obtained by Hückel. This acid on treatment with a mixture of hydrochloric and acetic acids at 200° yielded a new *perhydrodiphenic* acid, m. p. 220°.

Vocke (*loc. cit.*) reduced methyl diphenate over Raney nickel under pressure, using Adkins's procedure, to a mixture of perhydro- and hexahydro-esters. Waldeland, Zartman, and Adkins (*J. Amer. Chem. Soc.*, **1933**, **55**, 4234) had performed a similar reduction of ethyl diphenate, and had obtained a mixture of a solid and a liquid perhydro-ester. Professor Adkins kindly carried out a similar pressure reduction of the methyl ester on our behalf. We find that this product also is a mixture of stereoisomeric perhydro-esters. One of these is a solid, m. p. 73°, and this on hydrolysis yields the perhydro-acid of m. p. 220°, identical with that obtained by the inversion of Hückel's acid.

The liquid esters yielded a mixture of perhydro-acids, from which a form, m. p. 244°, was readily isolated, corresponding to the 245° acid of Vocke. This was identical with the acid already obtained from the oxidation of 9-ketoperhydrophenanthrene, m. p. 49°. The mixture also yielded the acid, m. p. 220°, already obtained from the solid ester, but we have so far not encountered the isomeride, m. p. 213°, reported by Vocke. One possibility is that Vocke's acid is an impure version of the 220° acid, but, against this, his acid gave an anhydride of m. p. 85° and no ketone, whereas the 220° acid behaves differently (see below). We prefer to leave this point open at present.

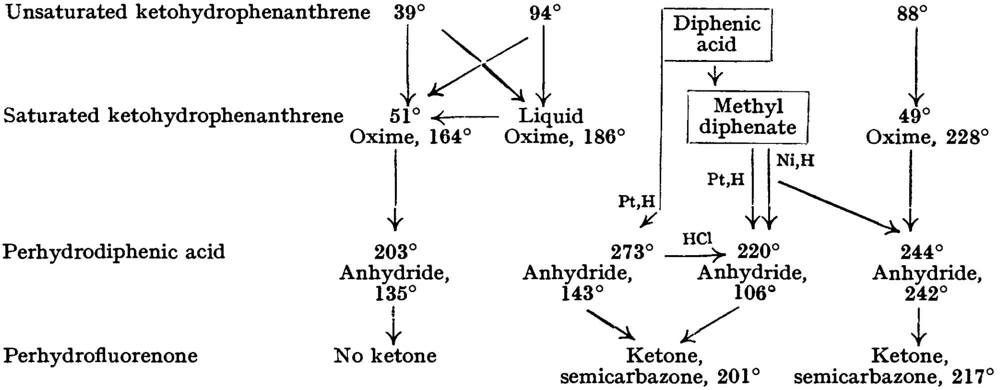
Catalytic hydrogenation of methyl diphenate over platinum also yielded the solid perhydro-ester, m. p. 73°, and thence the acid, m. p. 220°. This provides a convenient preparative method.

Formation of Ketones (VIII) *and Anhydrides* (IX).—The results are summarised below and discussed later.

203° *Acid.* This yielded a crystalline *anhydride*, m. p. 135°, when boiled with acetic anhydride. The anhydride evolved no carbon dioxide when heated at 350°, and at higher temperatures distilled mainly unchanged. No ketonic product could be isolated.

244° *Acid.* Treatment with acetic anhydride gave an oily anhydride, which deposited a few bold crystals, m. p. 117°. Crystallisation of the crude anhydride from benzene or acetic anhydride yielded a stable solid *anhydride*, m. p. 242°, which was also formed by heating the original oil to 170°. When the parent acid was heated alone at 310—320°, and then distilled, it yielded a perhydrofluorenone, which formed a semicarbazone, m. p. 216—217°. As regards the formation of ketone, our results tally with those of Vocke, but he reports two forms of the anhydride, m. p. 115° and 265°. This difference, and the existence of more than one form of the anhydride, remain to be explained.

273° *Acid.* With acetic anhydride this yielded an additive *compound*, m. p. 104°, which was shown to be the anhydride crystallised with one molecule of acetic anhydride. Vacuum sublimation of this gave the crystalline *perhydrodiphenic anhydride*, m. p. 143°. At 310° the acid yielded carbon dioxide and a perhydrofluorenone, the semicarbazone of which melted at 200—202° and appeared to be a mixture. Hückel's ketone, made by the Blanc procedure, gave a semicarbazone, m. p. 210°. Both semicarbazones were formed with difficulty.



220° *Acid.* The *anhydride*, m. p. 105—106°, was normal. At 310—315°, the acid yielded carbon dioxide and a ketone, giving a semicarbazone, m. p. 199—202°, identical with that obtained from the 273° acid.

213° *Acid.* According to Vocke, this yields a stable anhydride, m. p. 86°, and no ketone.

All the anhydrides are soluble crystalline compounds. Their molecular weights, determined by the micro-Rast method, are only slightly high for the unimolecular forms. There is no reason to suppose that they are other than unimolecular, except that the existence of several forms of the anhydride of the acid of m. p. 244° in some ways recalls the work of Hill (*J. Amer. Chem. Soc.*, 1930, **52**, 4110) on the simple and polymolecular anhydrides of adipic acid. In the absence of decisive experimental evidence, it is preferable to assume that this anhydride exists in one or more labile polymolecular modifications, rather than that the unimolecular form can exist in different stereoisomeric multiplanar modifications.

Our results are summarised in the diagram, where the numbers indicate melting points. At least one inactive form of perhydrodiphenic acid remains to be found.

DISCUSSION.

These results and those of previous workers show definitely that the applicability of the Blanc rule to acids of the adipic series is dependent on the degree of substitution and on the configuration, and it is of interest to examine how these factors may operate. For the sake of simplicity, the discussion may be confined to the formation of anhydrides and ketones by the Blanc procedure.

The formation of a pyro-ketone from an adipic acid must involve the following stages: (i) the coiling of the molecule into a form in which the carboxyl groups are within striking distance, (ii) the formation of anhydride, (iii) the decarboxylation of the anhydride with the production of ketone. The whole process may be accompanied by an inversion of configuration.

Under conditions allowing free rotation, the carboxyl groups of the perhydrodiphenic acids may be assumed to orient themselves at the furthest possible distance apart. It may easily be shown that the six isomerides will fall into three pairs according to the furthest possible divergence of the carboxyl groups. Whether the configuration of the backbone be *syn*- or *anti*-, the inter-carboxyl distances will be: *trans-trans*-acids > *cis-trans*-acids > *cis-cis*-acids. In all cases the distance will be less than that in a free zig-zag arrangement such as is possible in adipic acid itself. This factor must affect the ease of the formation of anhydride under Blanc conditions but cannot directly affect the ketonisation.

It is known from the work of Blanc, and of Farmer and Kracovski (J., 1927, 680), that many unimolecular adipic anhydrides have a considerable stability, and that the anhydride of αα′α′-tetramethyladipic acid can be heated to high temperatures without showing any tendency to pass into ketone. The anhydrides of the perhydrodiphenic acids are all stable at high temperatures, and in the two cases where no ketonisation occurs, exceptionally so. This may in part be due to the general effect of α-substitution.

The stability of the end-product is bound up with the possibility of configurational change. There would be a considerable difference in stability between the perhydrofluorenones formed without inversion from the various perhydrodiphenic acids. But the ketones possess a carbonyl group which is capable of enolisation from both lateral rings and therefore the configuration should theoretically be capable of inversion at both α-carbon atoms, only that of the backbone (*syn*- or *anti*-) being maintained. All the isomeric acids would therefore be expected to yield one of two tricyclic ketones, representing the final stable forms in the *syn*- and *anti*-series respectively. The perhydrofluorenone structure (VIII) consists of an α-hydrindanone unit fused by the β- and γ-carbon atoms to a *cyclo*hexane ring. In extension of the work of Hückel and collaborators on α-hydrindanone, it may be assumed that the forms of perhydrofluorenone containing *cis*-ring fusions will be more stable than those with *trans*-fusions. The final stable forms will therefore be *cis-syn-cis* and *cis-anti-cis*-, or *cis-trans*-mixtures rich in these isomerides.

This is borne out by the experimental results in so far as the 220° and 273° acids yield the same ketone (or mixture of ketones), whereas the 244° acid gives an isomeride. The question then arises: why do not the remaining two acids, m. p. 203° and 213°, behave similarly and give one or other of these ketones? We suggest that the reason lies in the mechanism of the inversion. There is no evidence that an inversion of configuration of the anhydride precedes ketone formation, and it seems more likely that the anhydride first yields the ketone of the same configuration, which subsequently undergoes inversion by enolisation at the high temperature of the reaction. If this is so, the determining factor will be the stability of the first-formed, unstable, ketone. Recent experimental work has shown that the formation of strained polycyclic ketones requires higher temperatures than does that of the corresponding unstrained ketones, both when inversion does and does not occur (Cook and Linstead, J., 1934, 946; Barrett and Linstead, J., 1935, 436), and that the strained ketones have the higher energy contents. It thus seems reasonable to suppose that the main reason for the inability of certain perhydrodiphenic acids, and similar acids derived from sterols, to yield ketones lies in the fact that the energy required for the formation of ketones of the same configuration is outside the range of the ordinary experimental conditions.

In conclusion, the most probable configuration for the known perhydrodiphenic acids may be indicated. The complete solution must await work in progress on their resolution and in other directions. The suggestions which follow are based on general analogies with the α-hydrindanone and α-decalone series.

1. The two acids, m. p. 203° and 213°, which fail to give ketones, have *trans-trans*-configurations, and between them account for the *trans-syn-trans*- and *trans-anti-trans*-isomerides.
2. The 273° and 220° acids belong to the same series with respect to the backbone, *i.e.*, they are both either *syn*- or *anti*-. The 273° acid, being inverted by acid, probably contains more *cis*-fusions than the 220° acid.
3. The 244° acid must belong to the opposite series with respect to the backbone, both because it gives a different ketone and because the first series already has its full complement of three isomerides.
4. The 203° and 244° acids have at least one *trans*-linking, as they are formed from ketoperhydrophenanthrenes with one *trans*-fusion (see preceding paper).

Hence we have :

	Cis-cis-.	*Cis-trans-.*	*Trans-trans-.*
Series 1 (*syn*- or *anti*-)	m. p. 273°	m. p. 220°	m. p. 203° or 213°
Series 2 (*anti*- or *syn*-)	—	m. p. 244°	m. p. 213° or 203°

The formation of wholly or predominantly *cis*-material by the hydrogenation of aromatic compounds over platinum tallies with common experience.

EXPERIMENTAL.

Perhydrodiphenic Acid, m. p. 203°.—9-Ketoperhydrophenanthrene (form 1), m. p. 51°, was reduced by the Ponndorf–Verley method (cf. Lund, *Ber.*, 1937, **70**, 1520). 9·8 G. of the ketone, mixed with 35 c.c. (80% excess) of M-aluminium *iso*propoxide, were heated so that one drop of *iso*propyl alcohol distilled in 10 seconds, the volume of solution being maintained by the addition of more of the alcohol. After about 8 hours, when no more acetone could be detected in the distillate, the contents of the flask were evaporated to dryness at 100°/10 mm. The residue was decomposed with dilute sulphuric acid, and the product isolated by means of ether. 9-*Hydroxyperhydrophenanthrene* (8·2 g.) boiled at 132°/0·5 mm. and set to a cheesy solid (Found : C, 81·2; H, 11·5. $C_{14}H_{24}O$ requires C, 80·7; H, 11·6%).

The *acetate*, b. p. 127°/1 mm., was prepared by boiling the alcohol with an excess of acetic anhydride for 2 hours (Found : C, 76·7; H, 10·2. $C_{16}H_{26}O_2$ requires C, 76·8; H, 10·5%).

Dehydration of 9-hydroxyperhydrophenanthrene over potassium hydrogen sulphate at 200° for 3 hours gave 75% of dodecahydrophenanthrene, A, b. p. 127°/13 mm.

The oxidation of the alcohol to a perhydrodiphenic acid was difficult, and the following procedure gave the best results. The alcohol (2·5 g.) was added to an ice-cold mixture of fuming nitric acid (15 c.c.) and concentrated nitric acid (45 c.c.). The reaction was started by gentle warming and moderated by ice-cooling. Finally the mixture was heated on the steam-bath for ½ hour, diluted with water, and cooled in ice. The sticky solid was collected on a filter, washed with water, and extracted with warm saturated sodium bicarbonate solution. The solution was extracted with ether, and the perhydrodiphenic acid was precipitated from the bicarbonate solution and dissolved in the minimum quantity of acetic acid. The *acid* separated in nodules, m. p. 193°, and after a number of crystallisations from 90% acetic acid it formed nodular masses of fine needles (0·7 g.), m. p. 202—203° (Found : C, 65·9, 66·2; H, 8·35, 8·55. $C_{14}H_{22}O_4$ requires C, 66·1; H, 8·75%).

The oxidation (i) of 9-ketoperhydrophenanthrene, m. p. 51°, with concentrated or with fuming nitric acid, (ii) of the acetate of the 9-hydroxy-compound by the procedure described above, (iii) of the unsaturated hydrocarbon, A, with permanganate under various conditions, yielded no solid perhydrodiphenic acid.

Perhydrodiphenic Acid, m. p. 243—244°.—1 G. of 9-ketoperhydrophenanthrene (form 3), m. p. 48°, was added to 5 c.c. of a 1 : 3 mixture of concentrated and fuming nitric acids, and the mixture warmed. The vigorous reaction was moderated by water-cooling, and completed by ½ hour's warming on the steam-bath. Solid separated during this process. The mixture was diluted with 5 c.c. of water and cooled in ice, and the crude acid filtered off. It was crystallised once from acetic acid with ice-cooling, and then repeatedly from acetone—which was necessary to remove traces of a higher oxidation product. The perhydrodiphenic acid (230 mg.) formed bright needles, m. p. 243—244° (bath initially at 235°) (Found : C, 65·8; H, 8·5. $C_{14}H_{22}O_4$ requires C, 66·1; H, 8·75%). In a larger experiment, the crude hydrogenation product from 38 g. of 9-ketododecahydrophenanthrene, m. p. 88°, was oxidised in this way and yielded 6·8 g. of the pure acid, m. p. 243°.

500 Mg. of the acid were heated in a sealed tube with 5 c.c. of glacial acetic acid and 2·5 c.c. of 10N-hydrochloric acid for 8 hours at 200°. The product was freed from tar with supernorit, and evaporated to dryness. The residue was fractionally crystallised from acetic acid, but only the starting material was recovered.

For another preparation of this acid, see below.

[With F. H. SLINGER.] *Diphenic Acid.*—The following method, suggested by Dr. A. W. Chapman, is a great improvement on the existing processes for preparing diphenic acid from phenanthraquinone or anthranilic acid. A mixture of phenanthraquinone (50 g.), acetic acid (150 c.c.), and hydrogen peroxide (500 c.c. of 20 vol.) was heated under reflux until a steady stream of bubbles was evolved, and this was maintained for 3 hours. The quinone had then disappeared and a white precipitate of diphenic acid had separated. The mixture was cooled and made alkaline. The liquid was filtered and acidified to Congo-red. In this way 87 g. of the quinone (from 100 g. of phenanthrene) yielded 71 g. of diphenic acid. Esterification by the Fischer–Speier method yielded the dimethyl ester, m. p. 73—74°.

Perhydrodiphenic Acids, m. p. 273° *and* 220°.—A solution of 5·5 g. of diphenic acid in 160 c.c. of purified acetic acid was shaken under hydrogen with 1·0 g. of Adams's catalyst. After 5 days, 1800 c.c. had been absorbed and hydrogenation ceased. A further 0·5 g. of catalyst was added, which led to the absorption of another 900 c.c.; and finally, after the addition of another 0·5 g. of catalyst, a total uptake of hydrogen of 3150 c.c. was reached (calc., 3050 c.c.). The sparingly soluble product slowly separated during the reduction. At the end the product was heated to boiling, and the catalyst removed by filtration. The solution then deposited 3·2 g. of perhydrodiphenic acid in microcrystalline plates, m. p. 273—274°, and another 0·5 g. was obtained from the mother-liquor (compare Hückel, *loc. cit.*).

1 G. of this acid was heated with 10 c.c. of glacial acetic acid and 5 c.c. of hydrochloric acid in a sealed tube at 200° for 8 hours. The product was filtered from a tarry by-product and evaporated to dryness. The residue was crystallised from acetic acid (charcoal) and yielded glistening needles of a *perhydrodiphenic acid* (0·52 g.), m. p. 219—220°. The m. p. was depressed by the isomeric acids, m. p. 203°, 244°, and 273° (Found : C, 65·6, 65·7; H, 8·5, 8·6. $C_{14}H_{22}O_4$ requires C, 66·1; H, 8·75%).

A solution of 10 g. of methyl diphenate in 250 c.c. of pure acetic acid was shaken in hydrogen with 1 g. of Adams's catalyst; 2600 c.c. were taken up in 5 days. A further 1 g. of catalyst was then added, and the hydrogenation continued until a total of 5450 c.c. had been absorbed in a total time of 8 days (calc., 4970 c.c.). After removal of the catalyst and solvent, the residue yielded 4·9 g. of *methyl perhydrodiphenate* in needles, m. p. 73°, and 4·2 g. of liquid ester. The solid ester depressed the m. p. of methyl diphenate (Found : C, 67·8; H, 9·2. $C_{16}H_{26}O_4$ requires C, 68·0; H, 9·3%). Hydrolysis of the solid ester with boiling 20% methyl-alcoholic potash was slow. The acid product had m. p. 220°, alone or in admixture with the acid described above, obtained by the inversion of the isomeride of m. p. 273°.

Reduction over Raney Nickel.—Professor Homer Adkins reports as follows : " 35 g. of methyl diphenate in 40 c.c. of methyl*cyclo*hexane were hydrogenated over Raney nickel at 150—300 atmospheres. Judged by the hydrogen absorption, hydrogenation was practically complete within less than 1 hour after the temperature reached 180°. Hydrogenation was allowed to proceed for 3 hours at 210—215°."

Removal of the solvent left a liquid, which slowly deposited 7·0 g. of needles. These had m. p. 73—74° after crystallisation from methyl alcohol and did not depress the m. p. of the solid methyl perhydrodiphenate (m. p. 73°) obtained by reduction over platinum. Hydrolysis yielded the acid of m. p. 220°.

The liquid residue yielded the following fractions: b. p. 134—136°/1 mm., 2 g.; 136—142°/1 mm., 5·6 g.; 142—145°/1 mm., 10·6 g.; 146—150°/1 mm., 2·7 g. The largest fraction had C, 68·7; H, 9·3 ($C_{16}H_{26}O_4$ requires C, 68·0; H, 9·3%), and hence was substantially methyl perhydrodiphenate. The fractions were hydrolysed separately with methyl-alcoholic potash, and the acids fractionally crystallised from dilute alcohol. The main product was an acid, m. p. 243—244°, identical with that already described, obtained by the oxidation of 9-ketoperhydrophenanthrene, m. p. 48°. No other acid of certain purity has as yet been isolated from these products.

Formation of Anhydrides and Ketones.—Acid, m. p. 203°. 500 Mg. of the acid were boiled for 5 hours with 5 c.c. of acetic anhydride. The excess of reagent was removed at 100°. The residue solidified on cooling, and pure *perhydrodiphenic anhydride*, m. p. 135°, was obtained by crystallisation from acetic anhydride, in glistening plates; yield, almost quantitative (Found: C, 70·8, 71·0; H, 8·2, 8·1; *M*, micro-Rast, 275. $C_{14}H_{20}O_3$ requires C, 71·1; H, 8·55%; *M*, 236). The anhydride dissolved in boiling 10% sodium hydroxide solution; on acidification the solution slowly deposited the original acid (m. p. and mixed m. p.).

The anhydride (350 mg., m. p. 135°) was heated in a slow current of nitrogen in a flask connected with a receiver, a drying tube, and a soda-lime tube for the measurement of evolved carbon dioxide. The temperature of the heating-bath was slowly raised from 250° to 350°. No carbon dioxide was evolved and after 1 hour only two drops of liquid distillate had collected. Further increase of the temperature led to the distillation of the anhydride (m. p. and mixed m. p.; identified also by hydrolysis to the parent acid, m. p. 203°). There was a trace of neutral distillate, but this failed to give a semicarbazone even on prolonged treatment. The soda-lime tube increased in weight by 12 mg. (calc. for complete ketonisation, 65 mg.), but some carbonisation occurred in the later stages, and this is of doubtful significance.

The parent acid (300 mg., m. p. 203°) was heated in a stream of nitrogen with 50 mg. of baryta. The temperature was slowly increased from 250° to 345°, held at this for 1 hour, and finally raised to 370° until nothing more distilled. The product was liquid in ice. After removal of acid and anhydride the neutral residue (80 mg.) yielded no semicarbazone. Yield of carbon dioxide, 35 mg. (calc., 52 mg.).

Acid, m. p. 244°. 500 Mg. of the acid were boiled for 5 hours with 5 c.c. of acetic anhydride. Removal of the excess of reagent, finally at 2 mm., left a viscous residue, which slowly deposited a few fine needles, m. p. 108—110°, and 117° after two crystallisations from acetic anhydride. This solid, after melting, resolidified at 160° and remelted at 239°. The viscous residue solidified when warmed with acetic anhydride and could only be brought into solution when boiled with a large excess of this solvent. It then separated in small rhombs, m. p. 241° (A). The *anhydride* was more soluble in boiling benzene and separated on slow evaporation of the solvent. After two crystallisations a constant m. p. of 242° was reached (B) (Found: C, 71·1; H, 9·1; *M*, 272. $C_{14}H_{20}O_3$ requires C, 71·1; H, 8·55%; *M*, 236). The original viscous anhydride slowly solidified when it was heated at 170°. After 15 minutes the material melted at 238° (C). All these preparations (A), (B), and (C) were identical. The anhydride (m. p. 242°) was insoluble in boiling 10% aqueous caustic soda, but was dissolved by warm 20% methyl-alcoholic potash. The solution yielded the acid of m. p. 244° (m. p. and mixed m. p.).

When the acid was treated with boiling acetyl chloride, it yielded a pasty solid from which only the anhydride of m. p. 242° could be isolated.

The acid (500 mg.) was heated alone in a current of nitrogen. At 310° to 320° a vigorous evolution of carbon dioxide occurred. When this subsided, the product was distilled at 335° and extracted with ether, and the extract washed with alkali and water. The perhydrofluorenone (400 mg.), after removal of the ether, was readily converted into semicarbazone, which was washed with light petroleum and crystallised from alcohol. It formed clusters of needles, m. p. 216—217°. Vocke (*loc. cit.*) gives m. p. 215° (Found: C, 67·7; H, 9·35. Calc. for $C_{14}H_{23}ON_3$: C, 67·4; H, 9·3%). During the ketonisation 89 mg. of carbon dioxide were evolved (calc., 87 mg.).

Acid, m. p. 273°. On treatment with acetic anhydride by the general method already described, a crude product was obtained, melting at about 140°. On crystallisation from acetic anhydride the m. p. fell to 100—103° and finally attained a constant value of 104°. The *compound* appears to be a perhydrodiphenic anhydride crystallising with one molecule of acetic anhydride (Found: C, 63·4, 63·4; H, 7·55, 7·3; *M*, micro-Rast, 158. $C_{18}H_{26}O_6$ requires C, 63·9; H, 7·7%; *M*, assuming complete dissociation in camphor, 169). After three sublimations under reduced pressure, pure *perhydrodiphenic anhydride* was obtained in glistening plates, constant m. p. 143° (Found : C, 71·2, 71·3; H, 8·5, 8·45; *M*, 295. $C_{14}H_{20}O_3$ requires C, 71·1; H, 8·55%; *M*, 236). Both products, m. p. 104° and 143°, dissolved readily in boiling 10% aqueous sodium hydroxide, and acidification of the solutions regenerated the original acid, m. p. 273°.

When the acid (400 mg.) was heated in a current of nitrogen, carbon dioxide was first evolved at about 310°, and ceased to come off after ½ hour at 310—315°. At 330° a yellow oil with a distinctive odour distilled. It was washed with alkali (residue, 280 mg.) and converted into semicarbazone. This did not form readily and the yield was poor even after 2 hours' heating on the steam-bath. The *perhydrofluorenone semicarbazone* formed clusters of flattened needles from alcohol, m. p. 200—202°, not improved by recrystallisation (Found : C, 67·9, 67·7; H, 9·25, 9·3. $C_{14}H_{23}ON_3$ requires C, 67·4; H, 9·3%). The carbon dioxide evolved weighed 62 mg., corresponding to 90% ketonisation.

Acid, m. p. 220°. The *anhydride*, made in the usual way, readily solidified; it crystallised from acetic anhydride in small plates, m. p. 105—106° (Found : C, 70·8; H, 7·95; *M*, 271. $C_{14}H_{20}O_3$ requires C, 71·1; H, 8·55%; *M*, 236). The anhydride dissolved in boiling 10% aqueous alkali; the solution regenerated the parent acid (m. p. and mixed m. p.) on acidification.

500 Mg. of the acid were heated alone for ½ hour at 310—315°. Carbon dioxide was readily evolved above 300°. The semicarbazone of the product, which formed slowly, had m. p. 199—201°, alone or in admixture with that prepared from the acid of m. p. 273°. The carbon dioxide evolved corresponded to 82% ketonisation.

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