

*The Synthesis of Some Perhydrophenanthrene Derivatives.*

By C. BUCHANAN and A. C. RITCHIE.

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Methods of preparation of *trans-as*-octahydro-9-oxophenanthrene have been investigated. *trans-anti-trans*-Perhydro-9-oxophenanthrene has been prepared from the corresponding perhydrodiphenic acid, and *cis-anti-trans*-perhydrophenanthrene-9:10-dicarboxylic acid has been obtained and its configuration established.

WHEN this work was undertaken three of the eight possible forms of perhydro-9-oxophenanthrene had been described (Linstead, Whetstone, and Levine, *J. Amer. Chem. Soc.*, 1942, **64**, 2014). Our intention was to obtain further isomers by hydrogenation of *trans-as*-octahydro-9-oxophenanthrene; but during our experiments similar work was published by Linstead and Whetstone (*J.*, 1950, 1428), and we discontinued ours. We now record some of our observations, and other experiments on perhydrophenanthrene derivatives.

The preparation of *trans-as*-octahydro-9-oxophenanthrene described by Blumenfeld (*Ber.*, 1941, **74**, 524) was thoroughly investigated. The first stage is a Diels-Alder reaction between 1-phenylbuta-1:3-diene and acraldehyde, which, it seems, gave mainly the *trans*-adduct. In later work on the analogous reaction with acrylic acid (Meek, Lorenzi, and Cristol, *J. Amer. Chem. Soc.*, 1949, **71**, 1830; Ropp and Coyner, *ibid.*, p. 1832; Alder, Vagt, and Vogt, *Annalen*, 1949, **565**, 135) the product had mainly the *cis*-configuration. In our experience the initial product is mainly the *cis*-adduct; this was shown by hydrogenation to a hexahydro-2-phenylbenzyl alcohol, which was purified by crystallisation of its hydrogen phthalate in >70% yield. The purified alcohol, m. p. 67–68°, was oxidised to *cis*-hexahydro-2-phenylbenzoic acid (Gutsche, *J. Amer. Chem. Soc.*, 1948, **70**, 4150). The *cis*-aldehyde is readily isomerised by alkali to the *trans*-form. Alder *et al.* (*loc. cit.*) suggest that previous workers had obtained *trans*-derivatives by inversion resulting from the formation of the bisulphite compound. We have found that inversion occurs on hydrolysis of the bisulphite compound by dilute acid or alkali, but the original *cis*-configuration of the aldehyde can be retained if the bisulphite compound is decomposed by formaldehyde.

Blumenfeld (*loc. cit.*) does not mention the use of a bisulphite compound, and moreover he reports that a small-scale hydrogenation with Raney nickel at atmospheric pressure and room temperature gave a hexahydro-2-phenylbenzyl alcohol whose 3:5-dinitrobenzoate melted at 101°. We find that the *cis*- and the *trans*-dinitrobenzoate melt at 108°

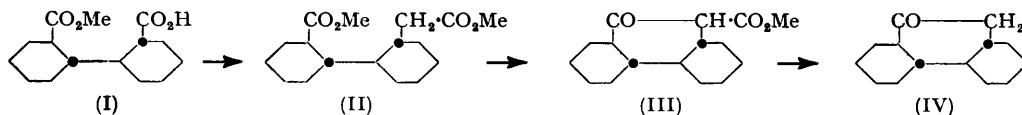
and 82° respectively. Thus the aldehyde obtained by Blumenfeld was the *cis*-isomer, and inversion must have occurred when it was hydrogenated at 180° with Raney nickel, presumably of low activity. As expected we found that hydrogenation at this temperature gave 2-cyclohexylhexahydrobenzyl alcohol, but at temperatures below 90° the benzene nucleus was unattacked.

When treated with phosphorus pentachloride in chloroform under the conditions described by Blumenfeld (*loc. cit.*), *cis*-hexahydro-2-phenylbenzyl alcohol gave only a hexahydrofluorene, whose structure was confirmed by dehydrogenation to fluorene. On similar treatment the *trans*-alcohol gave a product, which, on first distillation, had the b. p. quoted by Blumenfeld for the *trans*-chloride, but after a few seconds it became coloured, and when washed with dilute alkali and redistilled afforded the same hexahydrofluorene as the *cis*-alcohol. However, if all phosphorus compounds are first removed by prolonged washing with alkali the *trans*-chloride is obtained in good yield; it is converted into the hexahydrofluorene by distillation with phosphorus pentachloride. The hexahydrofluorene is identical with that obtained by Cook and Hewett (*J.*, 1936, 70) by a Clemmensen reduction of the hexahydrofluorenone obtained by cyclisation of the acid chloride of hexahydro-2-phenylbenzoic acid. The *cis*- and the *trans*-form of this acid give the same product in this reaction, but the *cis*-acid can also be readily cyclised by hydrogen fluoride or concentrated sulphuric acid, whereas the *trans*-acid cannot. The hexahydrofluorene and hexahydrofluorenone are thus almost certainly *cis*-compounds, as suggested by Braude and Forbes (*J.*, 1953, 2209).

*trans*-Hexahydro-2-phenylbenzyl chloride was readily converted into *trans*-2-phenylcyclohexylacetic acid (Blumenfeld, *loc. cit.*), which was also prepared by an Arndt-Eistert reaction with hexahydro-2-phenylbenzoic acid (Gutsche and Johnson, *J. Amer. Chem. Soc.*, 1946, 68, 2239). In the latter reaction we obtained better results by forming the amide or ester rather than the free acid. 2-Phenylcyclohexylacetic acid was also obtained in good yield from 1-phenylcyclohexene by bromination with *N*-bromosuccinimide followed by condensation of the crude bromo-compound with ethyl sodiomalonate. As 1-phenylcyclohexene has two allyl positions two products might be expected, but hydrolysis, decarboxylation, and hydrogenation of the crude product gave *cis*-2-phenylcyclohexylacetic acid in good yield. Although mainly the *cis*-acid, and hence *cis-as*-octahydro-9-oxophenanthrene are obtained, the *trans*-ketone can be formed by isomerisation with aluminium chloride (Cook, McGinnis, and Mitchell, *J.*, 1944, 286), and, as the yields are good, this affords a convenient method of preparing either ketone.

In our experiments on the hydrogenation of *trans-as*-octahydro-9-oxophenanthrene reduction was effected by the use of Adams platinum catalyst in ethanol, whereas Linstead and Whetstone (*loc. cit.*) found that addition of acetic acid was necessary to take hydrogenation beyond the octahydrophenanthrol stage. The main product in our experiments was, however, a liquid hydrocarbon corresponding to a perhydrophenanthrene, together with a few crystals of the *cis-anti-trans*-perhydro-9-hydroxyphenanthrene, m. p. 132°.

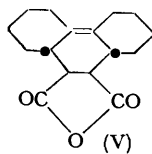
A possible route to the preparation of a perhydro-9-oxophenanthrene of known configuration from a known perhydrodiphenic acid was investigated. Methyl hydrogen *trans-anti-trans*-perhydrodiphenate (I) was converted into the corresponding perhydro-9-oxophenanthrene (IV) by the following stages:



All six possible perhydrodiphenic acids are known (Linstead, *J. Amer. Chem. Soc.*, 1942, 64, 1991); hence this synthesis might be capable of yielding other stereoisomeric modifications of the perhydrophenanthrene nucleus.

Another possible method of preparing a partially hydrogenated phenanthrene derivative, with substituents in the 9, or 9 and 10, positions suitable for conversion into a perhydrophenanthrene whose configuration could be established is a Diels-Alder reaction between

dicyclohex-1-enyl and a suitable dienophile; e.g., maleic anhydride gives  $\Delta^{12:13}$ -dodecahydrophenanthrene-9:10-dicarboxylic anhydride (V) (Gruber and Adams, *J. Amer. Chem. Soc.*, 1935, **57**, 2555). In this compound we should expect the hydrogen atoms on C<sub>(11)</sub> and C<sub>(14)</sub> to be *cis* to each other. Hydrogenation over Raney nickel at elevated temperature and pressure would be expected to give *trans*-addition and thus produce a *cis-anti-trans*-configuration. The corresponding perhydro-9-oxophenanthrenes had not been described when this work was in progress, but Linstead and Whetstone (*loc. cit.*) have since obtained one of the two possible forms of this compound.



Hydrogenation of the dimethyl ester from (V) gave a perhydrophenanthrene-9:10-dicarboxylic ester which was shown to have the *cis-anti-trans*-configuration by degradation to *cis-anti-trans*-perhydrodiphenic acid.

A similar route using acraldehyde in place of maleic anhydride seemed unpromising because of the low yield reported by Gruber and Adams (*loc. cit.*). The yield has been improved by a modified procedure, and this and other similar reactions are being further investigated.

### EXPERIMENTAL

*cis-Hexahydro-2-phenylbenzyl Alcohol*.—Crude 1:2:5:6-tetrahydro-2-phenylbenzaldehyde (68 g.), prepared from 1-phenylbuta-1:3-diene and acraldehyde (Blumenfeld, *loc. cit.*), was hydrogenated over Raney nickel (~8 g.) in ethanol (200 c.c.) at 90°/100 atm. After removal of the catalyst and solvent the residue (69 g.) distilled at 158–162°/12 mm. This material (53 g.) was heated at 100° for 3 hr. with phthalic anhydride (42 g.) in dry pyridine (30 c.c.). The product was dissolved in chloroform, and the solution was washed with dilute acid, and dried (Na<sub>2</sub>SO<sub>4</sub>), and the solvent was evaporated. Crystallisation of the residue from benzene gave *cis-hexahydro-2-phenylbenzyl hydrogen phthalate* (56 g.), m. p. 143–145°. A sample recrystallised from benzene had m. p. 145–146° (Found: C, 74.4; H, 6.7. C<sub>21</sub>H<sub>22</sub>O<sub>4</sub> requires C, 74.6; H, 6.5%). Hydrolysis with dilute sodium hydroxide solution gave *cis-hexahydro-2-phenylbenzyl alcohol*, b. p. 162–163°/13 mm., m. p. 67–68° (from light petroleum) (Found: C, 82.1; H, 9.4. C<sub>13</sub>H<sub>18</sub>O requires C, 82.1; H, 9.4%). The 3:5-dinitrobenzoate had m. p. 108–109° (Found: C, 62.2; H, 5.4; N, 7.4. C<sub>20</sub>H<sub>20</sub>O<sub>6</sub>N<sub>2</sub> requires C, 62.3; H, 5.2; N, 7.3%). Oxidation with chromic acid in acetic acid gave *cis-hexahydro-2-phenylbenzoic acid*, m. p. 76–77° (S-benzylthiuronium salt, m. p. 152–153°).

*trans-Hexahydro-2-phenylbenzyl Alcohol*.—*cis*-1:2:5:6-Tetrahydro-2-phenylbenzaldehyde (5 g.) was isomerised to the *trans*-form by keeping its solution in ethanol (20 c.c.), containing 1 c.c. of 10% aqueous sodium hydroxide, for 2½ days at room temperature. The *trans*-aldehyde (4 g.), b. p. 148–150°/10 mm., on hydrogenation under the same conditions as for the *cis*-form, gave *trans-hexahydro-2-phenylbenzyl alcohol* (2.9 g.), b. p. 155–160°/12 mm., m. p. 46–48°. The 3:5-dinitrobenzoate had m. p. 82° (Found: C, 62.1; H, 5.0; N, 7.6%) and the *hydrogen phthalate* m. p. 115–116° (Found: C, 74.9; H, 6.6%).

*cis- and trans-2-cyclohexylhexahydrobenzyl Alcohol*.—Hydrogenation of the *cis*-aldehyde (7 g.) in ethanol (100 c.c.) with Raney nickel (1 g.) at 150–160°/100 atm. for 3 hr. gave *cis-2-cyclohexylhexahydrobenzyl alcohol* (4.7 g.), b. p. 156–160°/10 mm., m. p. 62–63.5°. The 3:5-dinitrobenzoate had m. p. 145° (from ethanol) (Found: C, 61.2; H, 6.4. C<sub>20</sub>H<sub>26</sub>O<sub>6</sub>N<sub>2</sub> requires C, 61.5; H, 6.7%), and the *hydrogen phthalate* m. p. 132–133° (from benzene) (Found: C, 72.9; H, 8.1. C<sub>21</sub>H<sub>28</sub>O<sub>4</sub> requires C, 72.9; H, 8.1%). Oxidation with chromic acid in acetic acid gave *cis-2-cyclohexylhexahydrobenzoic acid*, m. p. 85° (Found: C, 74.1; H, 10.5. C<sub>13</sub>H<sub>22</sub>O<sub>2</sub> requires C, 74.3; H, 10.5%); its *p-nitrobenzyl ester* had m. p. 68° (Found: C, 69.6; H, 7.8; N, 4.3. C<sub>20</sub>H<sub>27</sub>O<sub>4</sub>N requires C, 69.6; H, 7.8; N, 4.1%). Similarly the *trans*-aldehyde gave the *trans*-alcohol, b. p. 160–162°/15 mm. [3:5-dinitrobenzoate, m. p. 112° (Found: C, 61.7; H, 6.9%)]. Oxidation gave *trans-2-cyclohexylhexahydrobenzoic acid*, b. p. 195°/15 mm. [*p-nitrobenzyl ester*, m. p. 70° (Found: C, 69.7; H, 7.6; N, 4.3%)].

*Hydrolysis of the Bisulphite Compound of cis-1:2:4:6-Tetrahydro-2-phenylbenzaldehyde*.—The bisulphite compound was boiled with 10% aqueous sodium carbonate (40 c.c.) for 2 hr., and the liberated aldehyde was extracted with ether. The extract was washed with water, dried (Na<sub>2</sub>SO<sub>4</sub>), and distilled. The fraction boiling at 158–163°/14 mm. gave, on hydrogenation, *trans-hexahydro-2-phenylbenzyl alcohol* (1.5 g.), which gave a dinitrobenzoate, m. p. 78–80°. Warming the bisulphite compound for 10 min. with dilute hydrochloric acid (30 c.c.) and treating the product as above gave the same alcohol (1.5 g.; 3:5-dinitrobenzoate, m. p. 79–82°).

Repetition of this procedure with 40% aqueous formaldehyde (20 c.c.) in place of hydrochloric acid gave finally the *cis*-alcohol (1.6 g.; 3 : 5-dinitrobenzoate, m. p. 108—109°).

*cis*-1 : 2 : 3 : 4 : 10 : 11-Hexahydrofluorene.—(a) To a suspension of phosphorus pentachloride (14.8 g.) in purified chloroform (30 c.c.) was added, gradually with shaking, a solution of *cis*-hexahydro-2-phenylbenzyl alcohol (11.4 g.) in chloroform (20 c.c.). After the initial vigorous reaction had moderated the mixture was heated on the water-bath for 2 hr., and distilled *in vacuo*. The fraction, b. p. 120—130°/13 mm., was washed with dilute sodium carbonate solution, dried, and redistilled, giving *cis*-1 : 2 : 3 : 4 : 10 : 11-hexahydrofluorene (7 g.), b. p. 120—123°/11 mm.,  $n_D^{18.5}$  1.5547 (Found : C, 90.4; H, 9.2. Calc. for C<sub>13</sub>H<sub>16</sub> : C, 90.6; H, 9.4%).

(b) This reaction was repeated with the *trans*-alcohol (1 g.), phosphorus pentachloride (1.3 g.), and chloroform (2.5 c.c.). The first few drops of distillate, after removal of the solvent and phosphorus oxychloride, had b. p. 140—150°/12 mm., but the residue darkened rapidly to a deep violet colour. Redistillation, after washing with dilute sodium carbonate solution, gave a pale mobile hydrocarbon (0.5 g.), b. p. 122—125°/13 mm.,  $n_D^{18.5}$  1.5541. The same hydrocarbon (0.5 g.) was obtained when *trans*-hexahydro-2-phenylbenzyl chloride (1 g.) was slowly distilled *in vacuo* with a little phosphorus pentachloride, and the distillate redistilled after being shaken with dilute sodium carbonate solution.

Dehydrogenation of the hydrocarbon with platinum at 260° gave fluorene, m. p. and mixed m. p. 112—113°.

*trans*-Hexahydro-2-phenylbenzyl Chloride.—The *trans*-alcohol (5 g.) in chloroform (25 c.c.) was added to phosphorus pentachloride (6.5 g.) in chloroform (13 c.c.), and the foregoing procedure was followed. After the solvent and most of the phosphorus oxychloride had been removed by warming under reduced pressure, the residue was shaken vigorously for 2 hr. with an excess of dilute sodium hydroxide solution. The mixture was extracted with ether, and the extract was washed with water, dried (Na<sub>2</sub>SO<sub>4</sub>), and distilled, giving *trans*-hexahydro-2-phenylbenzyl chloride (4.3 g.), b. p. 145—146°/12 mm. (Found : C, 74.5; H, 8.0. Calc. for C<sub>13</sub>H<sub>17</sub>Cl : C, 74.7; H, 8.2%).

*Cyclisation of cis- and trans-Hexahydro-2-phenylbenzoic Acid*.—Cyclisation of the *cis*-acid (1 g.) by the Friedel-Crafts reaction as described by Cook and Hewett (*loc. cit.*) gave finally the semicarbazone (1.05 g.) of *cis*-1 : 2 : 3 : 4 : 10 : 11-hexahydrofluoren-9-one, m. p. 205—206°. Recrystallisation from aqueous alcohol gave colourless needles, m. p. 213—214°, alone or mixed with the specimen prepared by Cook and Hewett. Similar treatment of the *trans*-acid (0.4 g.) gave the same semicarbazone (0.45 g.), m. p. 204—206°. Interaction of the *cis*-acid (0.5 g.) with hydrogen fluoride gave, after standard treatment, the same semicarbazone (0.6 g.; m. p. 204°), whereas the *trans*-acid was recovered unchanged.

The *cis*-acid (0.25 g.) afforded finally the same semicarbazone by warming with (a) concentrated sulphuric acid (2 c.c.) for a few seconds or (b) concentrated sulphuric acid (3 c.c.) and acetic acid (1 c.c.) for 15 min. The *trans*-acid, under conditions (a) or (b), gave no neutral product, and none of the acid could be recovered. With sulphuric acid (2 c.c.) and acetic acid (2 c.c.) no neutral product was obtained, and part of the *trans*-acid (0.05 g.) was recovered. Further dilution of the sulphuric acid by acetic acid gave complete recovery of the *trans*-acid.

*2-Phenylcyclohex-2-enylacetic Acid*.—1-Phenylcyclohexene and *N*-bromosuccinimide, in absence of a solvent, react violently with evolution of hydrogen bromide and formation of diphenyl. 1-Phenylcyclohexene (30.2 g.) was added, gradually with shaking, to a suspension of *N*-bromosuccinimide (34 g.) in carbon tetrachloride (100 c.c.). The mixture, protected from moisture by a calcium chloride tube, was gently warmed until a vigorous reaction set in and, when this had subsided, the mixture was boiled for 2 hr., left overnight in a refrigerator, and then filtered. The last traces of succinimide were removed from the filtrate by several washings with ice-cold dilute sodium hydroxide solution and with water. The solution was dried (Na<sub>2</sub>SO<sub>4</sub>) and distilled, giving 1-phenylcyclohexene (13 g.), b. p. 120°/12 mm., which deposited crystals of diphenyl (1.5 g.), m. p. 70°. The residue (14.5 g.), which could not be distilled without decomposition, was warmed with a suspension of ethyl sodiomalonate, prepared from ethyl malonate (2.78 g.), sodium (1.41 g.), and ethanol (19.6 c.c.). The product, after the normal treatment, gave ethyl 2-phenylcyclohex-2-enylmalonate (10 g.), b. p. 158—160°/0.3 mm. (Found : C, 71.7; H, 8.1. C<sub>19</sub>H<sub>24</sub>O<sub>4</sub> requires C, 71.9; H, 7.9%). Hydrolysis with potassium hydroxide (4 g.) in water (2 c.c.) and ethanol (10 c.c.) gave 2-phenylcyclohex-2-enylmalonic acid as plates (5.75 g.), m. p. 157—159° (decomp.) (from aqueous ethanol) (Found : C, 68.8; H, 6.5. C<sub>15</sub>H<sub>16</sub>O<sub>4</sub> requires C, 69.2; H, 6.15%). This acid was decarboxylated to 2-phenylcyclohex-2-enylacetic acid (3.4 g.), m. p. 116—118° (from light petroleum) (Found : C, 77.3; H, 7.3. C<sub>14</sub>H<sub>16</sub>O<sub>2</sub> requires C, 77.8; H, 7.4%).

Hydrogenation of the above acid over platinum in acetic acid gave *cis*-2-phenylcyclohexyl-acetic acid. Reduction of the unsaturated acid (0.48 g.) with sodium (2 g.) in boiling amyl alcohol (30 c.c.) gave, after the usual procedure, a pale brown solid (0.45 g.) which, on fractional crystallisation from benzene and light petroleum, gave *cis*-2-phenylcyclohexylacetic acid (8 parts; m. p. 168—169°) and the *trans*-isomer (1 part; m. p. 109—110°).

*Hydrogenation of trans-as-Octahydro-9-oxophenanthrene.*—The ketone was prepared by cyclisation of *trans*-2-phenylcyclohexylacetic acid by concentrated sulphuric acid or by hydrogen fluoride. Hydrogenation of the ketone (0.5 g.) in ethanol (30 c.c.) over platonic oxide (0.1 g.) at atmospheric pressure until 1 mol. of hydrogen had been absorbed (4 hr.) gave mainly *trans-as*-octahydro-9-phenanthrol (0.32 g.), m. p. 88—91° (from *n*-hexane), together with a small amount of the stereoisomer of m. p. 105° (Linstead, Whetstone, and Levine, *loc. cit.*, give m. p.s 90° and 100° respectively). When the reaction was repeated in more dilute solution with less catalyst (0.01 g.) the main product was the stereoisomer, m. p. 105°.

When the ketone (2 g.) and platonic oxide (0.1 g.) in ethanol (50 c.c.) were shaken with hydrogen at room temperature and atmospheric pressure, initial reduction was rapid but soon became slow, and further portions of catalyst were added during 4 days (to a total of 0.5 g.; hydrogen uptake 3.95 mols.). After removal of the catalyst and solvent, the residual oil was distilled, to give an almost quantitative yield of a clear liquid, b. p. 160—163°/11 mm. This was probably either *cis-syn-trans*-perhydrophenanthrene or a mixture of this with the *cis-anti-trans*-form (Found: C, 87.6; H, 12.4. Calc. for C<sub>14</sub>H<sub>24</sub>: C, 87.4; H, 12.6%). A few colourless needles, m. p. 131—132°, which were obtained by crystallisation of the residue from *n*-hexane, were probably identical with one of the *cis-anti-trans*-perhydro-9-phenanthrols (m. p. 133°) isolated by Linstead and Whetstone (*loc. cit.*).

*trans-anti-trans-Perhydro-9-oxophenanthrene from Perhydrodiphenic Acid.*—*trans-anti-trans*-Perhydrodiphenic acid was prepared by hydrolysis of the product of hydrogenation of methyl diphenate over Raney nickel at 230°/180 atm. The acid (10 g.) was heated with acetic anhydride (100 c.c.) for 20 hr., and the excess of the latter removed by distillation *in vacuo*. The crude anhydride was converted by sodium (3.14 g.) in methanol (150 c.c.) into the methyl hydrogen ester (8.5 g.), m. p. 152—154° (from aqueous acetic acid) (Found: C, 67.3; H, 8.9. C<sub>15</sub>H<sub>24</sub>O<sub>4</sub> requires C, 67.1; H, 8.9%). The half-ester was converted by an Arndt-Eistert reaction into methyl *trans-anti-trans*-2'-methoxycarbonylmethylidicyclohexyl-2-carboxylate (1.8 g.), b. p. 155—157°/0.8 mm. (Found: C, 68.7; H, 9.4. Calc. for C<sub>17</sub>H<sub>28</sub>O<sub>4</sub>: C, 68.9; H, 9.5%), which was converted as described by Bhattacharyya (*J. Indian Chem. Soc.*, 1945, **22**, 85) into *trans-anti-trans*-perhydro-9-oxophenanthrene (0.7 g.), b. p. 128—131°/2.8 mm. (oxime, m. p. 225—227°).

*cis-anti-trans-Perhydrophenanthrene-9:10-dicarboxylic Acid.*— $\Delta^{12:13}$ -Dodecahydrophenanthrene-9:10-dicarboxylic anhydride was prepared from dicyclohex-1-enyl and maleic anhydride (Gruber and Adams, *loc. cit.*). It was recovered unchanged after 3 hours' boiling with excess of methanol, and was esterified by the action of diazomethane on the acid. The *methyl ester* had m. p. 110° (from methanol) (Found: C, 70.7; H, 8.7. C<sub>18</sub>H<sub>26</sub>O<sub>4</sub> requires C, 70.6; H, 8.6%). Hydrogenation over Raney nickel at 190°/140 atm. for 2 hr. gave *dimethyl cis-anti-trans-perhydrophenanthrene-9:10-dicarboxylate*, m. p. 120° (from methanol) (Found: C, 70.1; H, 9.2. C<sub>18</sub>H<sub>28</sub>O<sub>4</sub> requires C, 70.1; H, 9.1%). The free acid, obtained by hydrolysis with alcoholic potassium hydroxide, had m. p. 164—166° (from benzene-light petroleum) (Found: C, 68.3; H, 8.7. C<sub>16</sub>H<sub>24</sub>O<sub>4</sub> requires C, 68.6; H, 8.6%).

The acid (320 mg.) was warmed with excess of thionyl chloride (3 c.c.) until evolution of hydrogen chloride had ceased. An excess of bromine (0.3 c.c.) was added, and heating continued for a further 3 hr. The excess of thionyl chloride and bromine was distilled off, finally *in vacuo*, water (10 c.c.) was added to the dark residue, and the mixture was heated for 2 hr. The dark brown granular solid, obtained on cooling, was separated and crystallised from aqueous methanol, to give *cis-anti-trans-9:10-dibromoperhydrophenanthrene-9:10-dicarboxylic acid* (360 mg.), m. p. 188—192° (decomp.) (Found: C, 43.6; H, 5.3. C<sub>16</sub>H<sub>22</sub>O<sub>4</sub>Br<sub>2</sub> requires C, 43.8; H, 5.0%). A solution of the dibromo-acid (210 mg.) in acetone (12 c.c.), with sodium iodide (210 mg.), was boiled for 2 hr., diluted with water and extracted with ether. The extract was washed with water, dried, and evaporated. Trituration of the residual gum with a little methanol, and crystallisation from light petroleum gave *cis-anti-trans- $\Delta^9:10$ -dodecahydrophenanthrene-9:10-dicarboxylic acid* (60 mg.), m. p. 167—168°. The same unsaturated acid was obtained by monobromination of the perhydro-ester with bromine in carbon disulphide in presence of a trace of iodine, followed by dehydrobromination with alcoholic potassium hydroxide. The unsaturated acid (125 mg.) was heated on the water-bath with concentrated nitric acid (1 c.c.)

and fuming nitric acid (2 c.c.), and the solution poured on crushed ice. The precipitated solid, on recrystallisation from light petroleum, gave *cis-anti-trans*-perhydrodiphenic acid (7 mg.), m. p. 202—203° (lit., 206°).

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UNIVERSITY OF GLASGOW.

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