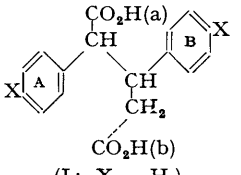
231. *Polycyclic Aromatic Hydrocarbons. Part XXXIV. Cyclisation of αβ-Diphenylglutaric Anhydride.*

By G. M. Badger, (Miss) J. E. Campbell, and J. W. Cook.

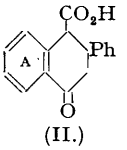
Cyclisation of the anhydride of αβ-diphenylglutaric acid (I) with aluminium chloride gave *α-phenyl-α-indan-3-on-1-ylacetic acid* (V) and not the expected tetralone (II), together with some 3-hydroxy-1 : 2-benzfluorenone (III). Treatment with caustic alkali partly converted this acid (V) into a *stereoisomeride*. Both acids have been transformed, by a series of reactions, into isomeric 1-*phenyltetrahydroacenaphthenes* (X), the structures of which have been established by conversion into (XI), through 1-*phenylacenaphthene*.

In connection with a project to synthesise dihydroxyperhydrochrysenes we have been interested in developing new routes to *s*-hexahydrochrysene derivatives which might serve as intermediates. The excellent method of Ramage and Robinson (*J.*, 1933, 607; 1938, 397) enables *s*-hexahydrochrysenes to be obtained in both *cis*- and *trans*-forms, but suffers from the disadvantage that poor yields are obtained in the preparation of the intermediate ββ′-diaryladipic acids. It seemed possible that derivatives of 3-phenyltetral-1-one-4-carboxylic acid (II) suitable for our purpose could be obtained by cyclisation of αβ-diarylglutaric acids (I, I*a*), which are readily available by the Michael condensation of arylacetic esters with arylcinnamic esters. αβ-Diphenylglutaric acid (I) is known in all four possible optically active forms (Avery and Maclay, *J. Amer. Chem. Soc.*, 1929, **51**, 2833), the two (±)-forms having m. p.s 231° and 208°. The higher-melting acid is obtained preferentially by the Michael reaction between ethyl phenylacetate and ethyl cinnamate, and we have found that it is readily converted by acetic anhydride into the anhydride of the lower-melting acid.

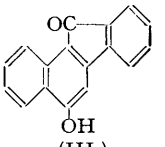
When this anhydride was treated with anhydrous aluminium chloride in nitrobenzene solution, it was transformed into a keto-acid. From the work of von Braun and his collaborators (see Johnson, " Organic Reactions," Vol. II, p. 116), who showed that such cyclisations give six- in preference to five-membered rings, it was to be expected that this keto-acid would have the desired structure (II). Some support was lent to this view by the fact that when the internal Friedel–Crafts reaction was conducted without ice-cooling there was also isolated a small amount of a bright red ketone which was shown to be 3-hydroxy-1 : 2-benzfluorenone (III). This was identified by conversion into its acetate and into 3-acetoxy-1 : 2-benzfluorene (Cook and Preston, *J.*, 1944, 559), and it could clearly arise by further cyclisation of (II) followed by dehydrogenation under the influence of aluminium chloride.



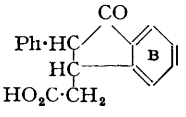
(I; X = H.)
(I*a*; X = OMe.)



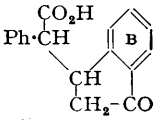
(II.)



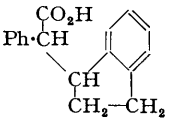
(III.)



(IV.)



(V.)



(VI.)

When, however, the chloride of the pure keto-acid was treated with aluminium chloride (III) was not formed, and the keto-acid itself was unaffected by anhydrous hydrogen fluoride. This cast doubt on the validity of the assumption that the keto-acid formed from the anhydride of (I) was represented by the structure (II), and further investigation showed that the reaction had in fact given, not the tetralone derivative (II), but an indanone derivative (V). Five-membered

ring formation involves reaction of ring B of (I) rather than ring A, and could lead to two alternative structures, (IV) or (V), depending upon which carboxyl group furnishes the carbonyl group. Structure (IV) was excluded, for the keto-acid gave a *benzylidene* derivative.

Intramolecular acylation may lead to a five-membered ring when an alternative six-membered ring is possible if there are activating substituents in the aromatic ring which is concerned in the process. This result does not seem to have been observed hitherto in the cyclisation of saturated acids in the absence of such activation, although it is known that if unsaturation is present in the carbon chain five-membered rings may be formed preferentially (compare Stobbe and Vieweg, *Ber.*, 1902, **35**, 1727; Haworth and Sheldrick, *J.*, 1935, 636; Cook and Preston, *loc. cit.*). There appears to be no reason why cyclisation of the carboxyl group (*b*) in (I) on to ring A should be inhibited by steric influences, and it is probable that the determining factor is a deactivation of ring A by the carboxyl group (a). It is consistent with what is known of the rapidity with which an inductive effect becomes damped in passing along a saturated carbon chain that the deactivating effect of this carboxyl group on ring (A), which requires transmission through only one carbon atom, completely outweighs the deactivating effects of both carboxyl groups on ring (B). Such effects would have to be transmitted through two saturated carbon atoms.

The formation of (V) to the exclusion of (IV) is also of interest. This involves cyclisation of carboxyl group (b), adjacent to a secondary carbon atom, on to ring B, rather than cyclisation of carboxyl group (a), which adjoins a tertiary carbon atom. Analogous effects have been observed by Haworth (*J.*, 1932, 1128), who found that in the Friedel–Crafts reaction between naphthalene and methylsuccinic anhydride in nitrobenzene solution the carboxyl group which adjoins the methylene group becomes attached to the aromatic nucleus, and by Robinson and Young (*J.*, 1935, 1414), who record a similar result in the condensation of phenylsuccinic anhydride with veratrole, also in nitrobenzene solution. Superficially, this might be compared with the similar orientating influence of the methyl group and the phenyl group (to which attention has been drawn, for example, by Grieve and Hey, *J.*, 1933, 968), in spite of the circumstance that the methyl group is electron-repelling and the phenyl group is intrinsically electron-attracting (compare Ingold, *Chem. Reviews*, 1934, **15**, 239). Such an interpretation would, however, be an unwarranted generalisation, inconsistent with other recorded results.

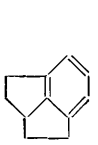
Thus, phenylsuccinic anhydride reacts with benzene at the carboxyl group adjacent to the tertiary carbon atom (Anschütz, Hahn, and Walter, *Annalen*, 1907, **354**, 148) whereas 2 : 4-dimethoxyphenylsuccinic anhydride and resorcinol dimethyl ether give about equal amounts of the two isomeric keto-acids (Rice, *J. Amer. Chem. Soc.*, 1931, **53**, 3159). Mixtures of isomerides are also formed in the Friedel–Crafts reaction between methylsuccinic anhydride and benzene or toluene (Mayer and Stamm, *Ber.*, 1923, **56**, 1424). It is to be noted that in none of the cases just cited was nitrobenzene used as a solvent. Possibly this influences the course of the reactions, for it is known that in Friedel–Crafts reactions with naphthalene and phenanthrene and their derivatives the nature of the solvent has considerable influence in determining the positions of substitution.

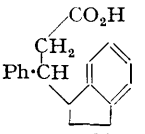
The structure of the product of cyclisation of (I) as *α-phenyl-α-indan-3-on-1-ylacetic acid* (V) was established by a series of transformations which we have carried out. This keto-acid (designated as isomeride-A) was dimorphic and had m. p.s 154—155° and 170—171°. Hydrolysis of its *methyl* ester with alcoholic alkali gave not only the original acid but also an isomeric *keto-acid* (isomeride-B), m. p. 225—226°. The higher-melting acid was likewise formed by the prolonged action of boiling aqueous-alcoholic alkali on the lower-melting acid. Only isomeride-B was isolated from the hydrolysis of its *methyl* ester, but some isomeride-A may have been present in the non-crystalline acidic material which was also formed. Clearly the two keto-acids are stereoisomeric.

Clemmensen reduction of these gave, respectively, *α-phenyl-α-1-indanylacetic acid*-A and *α-phenyl-α-1-indanylacetic acid*-B, both of which may be represented by structure (VI). The former acid (VIA) could not be dehydrogenated with sulphur or palladium, and it was recovered unchanged after attempted cyclisation with anhydrous hydrogen fluoride; an internal Friedel–Crafts reaction gave a non-acidic gum without carbonyl reactivity. Attempted dehydrogenation with palladium of the homologue (VIII) described below was also unsuccessful. These negative results are in accord with the structure (V) for the keto-acid from which (VI) was obtained, but cannot be reconciled with structure (II) which should give a naphthalene derivative by dehydrogenation of the reduced acid, and the latter should undergo ready cyclisation to a tetrahydrobenzfluorenone. On the other hand, dehydrogenation of (VI) would not be expected under the conditions used, and the failure to undergo cyclisation is in harmony with previous failures to

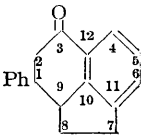
prepare the highly strained tricyclic system (VII) which would be present in the only cyclic ketone that (VI) could give (compare v. Braun *et al.*, *Ber.*, 1917, **50**, 56; 1928, **61**, 956; 1929, **62**, 145).

Chain lengthening of the stereoisomeric acids (VI) by the Arndt–Eistert procedure gave β-*phenyl*-β-1-*indanylpropionic acid*-A and β-*phenyl*-β-1-*indanylpropionic acid*-B (VIII). It was not found possible to convert this A-acid into the stereoisomeride (B) by prolonged boiling of its methyl ester with alkali. The two acids were cyclised by anhydrous hydrogen fluoride to

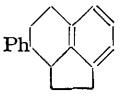

(VII.)



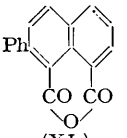
(VIII.)



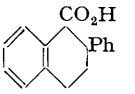
(IX.)



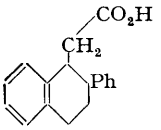
(X.)



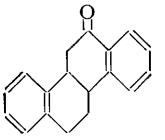
(XI.)



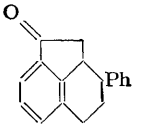
(XII.)



(XIII.)



(XIV.)



(XV.)

stereoisomeric 3-*keto*-1-*phenyl*-1 : 2 : 3 : 9-*tetrahydroacenaphthenes* (IX, A and B). Cyclisation of the acid-A (VIII) was also accomplished by treatment of its chloride with aluminium chloride or stannic chloride.

Reduction of the ketone-A (IX) by Clemmensen's method gave 1-*phenyl*-1 : 2 : 3 : 9-*tetrahydroacenaphthene*-X (X), m. p. 71°, but reduction by the Huang–Minlon modification (*J. Amer. Chem. Soc.*, 1946, **68**, 2487) of the Wolff–Kishner method gave in addition an isomeric 1-*phenyl*-1 : 2 : 3 : 9-*tetrahydroacenaphthene*-Y (X), m. p. 59°. Reduction of ketone-B (IX) by the latter method gave only 1-phenyltetrahydroacenaphthene-Y. The isomerisation of ketone-A during alkaline reduction is surprising and difficult to interpret in view of the remoteness of the carbonyl group from an asymmetric centre. The possibility is not excluded that in one of the hydrocarbons the ring carrying the phenyl group has become aromatic owing to double-bond migration.

Both hydrocarbons (X) were smoothly dehydrogenated to the same 1-*phenylacenaphthene*, the structure of which was confirmed by oxidation to the known 2-phenyl-1 : 8-naphthalic anhydride (XI).

The isolation of two parallel series of stereoisomerides of (V), (VI), (VIII), (IX), and (X) provides decisive evidence in favour of structure (V) for the cyclisation product of (I) and constitutes the final link in the chain of evidence against structure (II). If the latter structure were correct then its reduction product would be (XII) and the subsequent homo-acid (XIII). Newman (*J. Amer. Chem. Soc.*, 1938, **60**, 2947) has synthesised the *cis*-form of (XIII) and has cyclised it to *cis*-2-ketohexahydrochrysene (XIV). From the work of Ramage and Robinson (*loc. cit.*) it is to be expected that the *trans*-form of (XIII) would cyclise to the unknown *trans*-2-ketohexahydrochrysene (XIV), but the possibility that steric factors might lead to (XV) cannot be excluded, and reduction of (XV) would give the structure (X) which results from the route through (V). The isolation of two stereoisomeric homologues of (V) effectively disposes of this possibility, for if the alternative structure (XIII) were correct one of the isomerides would necessarily be Newman's *cis*-acid and would cyclise to his *cis*-ketone (XIV). This possibility is excluded by m. p. comparisons with our products.

Experimental.

αβ-Diphenylglutaric Anhydride.—Condensation of ethyl phenylacetate (100 g.) and ethyl cinnamate (100 g.) by heating under reflux for 2½ hours with sodium ethoxide (from 4 g. of sodium and 60 c.c. of ethanol) (compare Borsche, *Ber.*, 1909, **42**, 4496) gave a theoretical yield of αβ-diphenylglutaric esters, from which the higher-melting isomeride (140 g.) was isolated by recrystallisation from ethanol.

Hydrolysis with potassium hydroxide (175 g.) in boiling 50% ethanol (2340 c.c.) for 9 hours gave αβ-diphenylglutaric acid, m. p. 230—231° (110 g.). This acid was heated under reflux for 8 hours with acetic anhydride (500 c.c.). After concentration under reduced pressure, αβ-diphenylglutaric anhydride was collected and recrystallised from chloroform–light petroleum. It formed colourless crystals, m. p. 125—126° (90 g.). Avery and Maclay (*loc. cit.*), who prepared the anhydride from the same acid by heating under pressure with acetyl chloride, give m. p. 126·5°.

α-Phenyl-α-indan-3-on-1-ylacetic Acid-A (V).—Aluminium chloride (40 g.) was added gradually to a stirred ice-cold solution of αβ-diphenylglutaric anhydride (35 g.) in nitrobenzene (400 c.c.). After the addition was complete, the stirred mixture was allowed to warm to room temperature, and the reaction was then allowed to proceed for 60 hours. After decomposition with ice and hydrochloric acid, the nitrobenzene was removed in steam and the residue recrystallised from methanol. *α-Phenyl-α-indan-3-on-1-ylacetic acid*-A, thus obtained, formed colourless needles, m. p. 154—155° (20 g.) (Found : C, 76·4; H, 5·1. $C_{17}H_{14}O_3$ requires C, 76·7; H, 5·3%). A fused specimen, after resolidification, was found to have m. p. 170—171°, and the specimen, m. p. 154—155°, was also converted into the higher-melting form by prolonged heating at 100°. The higher-melting form (Found : C, 77·0; H, 5·6%) was also obtained by recrystallisation from ethyl acetate. Three recrystallisations of the higher-melting form from methanol, gave the lower-melting form.

The 2 : 4-*dinitrophenylhydrazone* formed orange-red needles from acetic acid, m. p. 261° (decomp.) (Found : C, 62·0; H, 4·1. $C_{23}H_{18}O_6N_4$ requires C, 61·9; H, 4·1%). The *benzylidene* derivative crystallised from acetic acid in pale yellow prisms, m. p. 185—186° (Found : C, 81·1; H, 5·3. $C_{24}H_{18}O_3$ requires C, 81·4; H, 5·1%). The *methyl* ester, prepared from the acid with methanol and dry hydrogen chloride, formed colourless needles (from methanol), m. p. 99—100° (Found: C, 76·75; H, 5·5. $C_{18}H_{16}O_3$ requires C, 77·1; H, 5·75%).

α-Phenyl-α-indan-3-on-1-ylacetic Acid-B.—The above methyl ester (1·2 g.) was hydrolysed by heating under reflux for 1 hour with potassium hydroxide (2 g.) in ethanol (15 c.c.) and water (5 c.c.). The solution became highly coloured, sometimes dark red, blue, or green. Addition of hydrochloric acid gave a gummy precipitate which was crystallised from methanol. The first crop (0·1 g. to 0·3 g. in different runs) was recrystallised and gave *α-phenyl-α-indan-3-on-1-ylacetic acid*-B as colourless crystals, m. p. 225—226° (Found : C, 76·8; H, 5·2%). A small amount of the original acid, m. p. 154—155° was also obtained from the liquors, but the yield of the two crystalline products never exceeded 50%, the remainder being an uncrystallisable gum. The new acid, m. p. 225—226°, was also obtained, in small yield, when the acid, m. p. 154—155°, was heated under reflux with potassium hydroxide in aqueous alcohol for various periods.

The *methyl* ester of the acid, m. p. 225—226°, was prepared with methanolic hydrogen chloride. It formed colourless prisms (from methanol), m. p. 138—139° (Found : C, 77·2; H, 5·8%). Hydrolysis of this ester gave only the higher-melting acid in crystalline form, together with an oily acidic material.

The 2 : 4-*dinitrophenylhydrazone* of the acid formed orange needles, m. p. 284—285° (decomp.) (from nitrobenzene) (Found : C, 61·7; H, 3·9%).

3-*Hydroxy*-1 : 2-*benzfluorenone* (III).—This was obtained in an experiment in which aluminium chloride was added to a solution of αβ-diphenylglutaric anhydride in nitrobenzene, without ice-cooling. Recrystallisation of the crude acidic product gave a small amount (0·12 g.) of red insoluble material. It was almost insoluble in benzene, acetone, and methanol, but was recrystallised from a large volume of acetic acid. Sublimation at 210°/0·5 mm., and recrystallisation from acetic acid, gave red needles, m. p. 304—310° (decomp.). They gave a violet-red solution in dilute sodium hydroxide, being reprecipitated by acid, and a green solution in concentrated sulphuric acid. These properties are in conformity with the formulation of the compound as 3-hydroxy-1 : 2-benzfluorenone (Found : C, 82·8; H, 4·2. Calc. for $C_{17}H_{10}O_2$: C, 82·9; H, 4·1%). It was further identified by acetylation with acetic anhydride to give 3-acetoxy-1 : 2-benzfluorenone, m. p. 185—186°, and by reductive acetylation to give 3-acetoxy-1 : 2-benzfluorene, m. p. 157—158°. Both acetyl compounds were identified by direct comparison with authentic specimens (Cook and Preston, *loc. cit.*; Fierz-David and Jaccard, *Helv. Chim. Acta*, 1928, **11**, 1042).

α-Phenyl-α-1-indanylacetic Acid-A (VI).—Water (18 c.c.), concentrated hydrochloric acid (44 c.c.), toluene (25 c.c.), α-phenyl-α-indan-3-on-1-ylacetic acid-A (2·5 g.), and acetic acid (5 c.c.) were added, in the order named, to granulated amalgamated zinc (compare Martin, *J. Amer. Chem. Soc.*, 1936, **58**, 1438) and the mixture was heated under reflux vigorously for 24 hours. Further portions (each of 12·5 c.c.) of concentrated hydrochloric acid were added at intervals of 6 hours. The product (10 g.), which crystallised from the toluene on cooling and from a benzene extract of the aqueous layer on concentration, was recrystallised from benzene–light petroleum (b. p. 60—80°). *α-Phenyl-α-1-indanylacetic acid*-A formed colourless needles, m. p. 141—142° (Found : C, 81·0; H, 6·3. $C_{17}H_{16}O_2$ requires C, 81·0; H, 6·4%).

α-Phenyl-α-1-indanylacetic Acid-B.—α-Phenyl-α-indan-3-onylacetic acid-B (m. p. 225—226°) was reduced as above, except that (owing to the insolubility of the acid) anisole was used instead of toluene. *α-Phenyl-α-1-indanylacetic acid*-B formed colourless prisms, m. p. 153—154° (from benzene) (Found : C, 81·1; H, 6·1%).

β-Phenyl-β-1-indanylpropionic Acid-A (VIII).—A mixture of ice-cold anhydrous benzene (8 c.c.), pyridine (2 drops), thionyl chloride (5 c.c.), and α-phenyl-α-1-indanylacetic acid-A (1·25 g.) was allowed to warm to room temperature during ½ hour, and was then warmed to 40° for ½ hour. The excess of thionyl chloride and benzene were removed in a vacuum on the water-bath. The residue, dissolved in a little benzene, was decanted from the pyridine hydrochloride and added dropwise to an ethereal solution (*ca.* 200 c.c.) of diazomethane (from 3 g. nitrosomethylurea; *Org. Synth.*, Coll. Vol. 2, p. 165), previously dried over potassium hydroxide pellets. During the addition, the flask was cooled in a freezing mixture, and the contents stirred mechanically. After a further ½ hour's stirring, the solution was left overnight. The solvent was allowed to evaporate spontaneously, and the yellow residue was dissolved in dioxan (15 c.c.) and heated on the water-bath with 20% ammonium hydroxide (20 c.c.) and 10% aqueous silver nitrate (10 c.c.) until evolution of nitrogen was complete. A silver

mirror normally formed on the walls of the vessel. The mixture was then boiled with charcoal, and filtered. *β-Phenyl-1-β-indanylpropionamide* (0·9 g.) formed colourless needles, from alcohol, m. p. 151—152° (Found: C, 81·5; H, 7·1; N, 5·5. $C_{18}H_{19}ON$ requires C, 81·5; H, 7·2; N, 5·3%). Hydrolysis of the amide (1 g.) was effected by 12 hours' boiling with potassium hydroxide (1 g.) in alcohol (25 c.c.) and water (2 c.c.). *β-Phenyl-β-1-indanylpropionic acid*-A formed colourless prisms, m. p. 123—125° (from dilute acetic acid) (Found: C, 81·3; H, 6·7. $C_{18}H_{18}O_2$ requires C, 81·2; H, 6·8%).

β-Phenyl-β-1-indanylpropionic Acid-B.—α-Phenyl-α-1-indanylacetic acid-B was converted into the acid chloride and treated with diazomethane as described for the above isomeride-A. In this case, however, it was found preferable to isolate the *diazo-ketone*. It formed yellow needles (from benzene), m. p. 126—128° (decomp.) (Found: N, 10·2. $C_{18}H_{16}ON_2$ requires N, 10·2%). Attempts to prepare a crystalline amide or ester from this product were unsuccessful. It was found, however, that a pure acid could be obtained from a crude ester, and the following procedure was adopted. The diazo-ketone (0·5 g.) in methanol (18 c.c.) was treated with a slurry of silver oxide (from 2 g. of silver nitrate) and methanol (10 c.c.), in portions. When the reaction had subsided, the mixture was heated under reflux for 1 hour, boiled with charcoal, and filtered. The filtrate was concentrated to 15 c.c., and potassium hydroxide (1·25 g.) was added. After heating under reflux for 1 hour, the mixture was acidified, and extracted with ether. The oil obtained on removal of the ether crystallised from light petroleum to which a little chloroform was added. Further crystallisation from light petroleum gave *β-phenyl-β-1-indanylpropionic acid*-B (0·2 g.) as small colourless prisms, m. p. 104—105° (Found: C, 81·2; H, 6·6%).

3-*Keto*-1-*phenyl*-1 : 2 : 3 : 9-*tetrahydroacenaphthene*-A (IX).—(i) The above phenylindanylpropionic acid-A (1 g.) was treated with excess of thionyl chloride and benzene in the usual way, and the solution evaporated in a vacuum. The product, in dry benzene (16 c.c.), was treated at room temperature with aluminium chloride (0·6 g.) in portions. The temperature was kept between 30° and 50° for 3 hours, after which the mixture was decomposed with ice and hydrochloric acid. Removal of the benzene gave 3-*keto*-1-*phenyl*-1 : 2 : 3 : 9-*tetrahydroacenaphthene*-A (0·6 g.), which formed small colourless prisms, m. p. 101—102° (from alcohol) (Found: C, 87·0; H, 6·2. $C_{18}H_{16}O$ requires C, 87·1; H, 6·5%).

The 2 : 4-*dinitrophenylhydrazone* formed small scarlet prisms, from chloroform, m. p. 249—250° (Found: C, 67·4; H, 4·5. $C_{24}H_{20}O_4N_4$ requires C, 67·3; H, 4·7%).

The same ketone (0·75 g.) was obtained (ii) when the acid (1 g.) was treated with anhydrous hydrogen fluoride, and the reagent allowed to evaporate from a platinum crucible fitted with a lid; and also (iii) when stannic chloride (0·5 c.c.) in dry benzene (0·5 c.c.) was added to a solution of the acid chloride (from the acid, 0·5 g.; benzene, 5 c.c.; and phosphorus pentachloride, 0·45 g.).

3-*Keto*-1-*phenyl*-1 : 2 : 3 : 9-*tetrahydroacenaphthene*-B (IX).—Cyclisation of phenylindanylpropionic acid-B with hydrogen fluoride was carried out as described for the A-isomeride. 3-*Keto*-1-*phenyl*-1 : 2 : 3 : 9-*tetrahydroacenaphthene*-B formed colourless prisms, m. p. 139—140°, from alcohol (Found: C, 86·9; H, 6·3%). Its 2 : 4-*dinitrophenylhydrazone* formed small dark red prisms, m. p. 229—230°, from chloroform (Found: C, 67·3; H, 4·7%).

1-*Phenyl*-1 : 2 : 3 : 9-*tetrahydroacenaphthene* (X).—(i) The above ketone-A (1 g.) and hydrazine hydrate (0·5 c.c.; 85%) were added to a solution of sodium (0·25 g.) in ethylene glycol (10 c.c.). After 1 hour's heating under reflux, the condenser was removed, and the heating continued until the temperature of the contents of the flask reached 195—200°. Refluxing was then continued for 3 hours. After cooling, the mixture was acidified and extracted with benzene. Removal of the solvent and recrystallisation from alcohol gave a first crop of 1-*phenyltetrahydroacenaphthene*-Y (X) which after further recrystallisation formed long colourless needles, m. p. 59—60° (Found: C, 92·1; H, 8·0. $C_{18}H_{18}$ requires C, 92·3; H, 7·7%). Concentration of the liquors gave a mixture of the above needles together with some hexagonal prisms. The latter were separated by hand, and on recrystallisation from methanol, 1-*phenyltetrahydroacenaphthene*-X (X) was obtained as colourless prisms, m. p. 71—72° (Found: C, 92·3; H, 7·5%). A mixed m. p. with the Y-isomeride was 38—42°.

(ii) A small yield of the X-isomeride was also obtained by reduction of the ketone-A by the Clemmensen method. The m. p. (68—70°) was not depressed by admixture with the specimen obtained as above. A mixture of this hydrocarbon with a specimen of *cis*-hexahydrochrysene (XIV), m. p. 73—74°, had m. p. 40—45°.

(iii) The above ketone-B, when reduced by the Wolff–Kishner method as described for the ketone-A, gave only 1-phenyltetrahydroacenaphthene-Y, which was identified by direct comparison with the specimen obtained as above. No trace of the X-isomeride was observed.

1-*Phenylacenaphthene*.—1-Phenyltetrahydroacenaphthene-Y (0·34 g.) was dehydrogenated by heating at 290—300° with palladium black (0·05 g.) in an atmosphere of carbon dioxide until no more hydrogen was evolved (4 hours). 1-*Phenylacenaphthene* (0·2 g.) formed colourless leaflets, m. p. 105—106° (Found: C, 93·8; H, 6·0. $C_{18}H_{14}$ requires C, 93·9; H, 6·1%).

Dehydrogenation of 1-phenyltetrahydroacenaphthene-X was carried out in the same way, and the product was shown by mixed m. p. to be identical with that obtained above.

2-*Phenyl*-1 : 8-*naphthalic Anhydride*.—A solution of the above 1-phenylacenaphthene (0·2 g.) in acetic acid (3·5 c.c.) was treated with sodium dichromate (1·4 g.) slowly, and with shaking. The mixture was heated under reflux for 2 hours, poured into warm water, cooled, and filtered. Extraction with boiling sodium carbonate solution containing a little sodium hydroxide, precipitation with acid, and sublimation at 240° at ordinary pressure gave 2-phenyl-1 : 8-naphthalic anhydride as pale yellow crystals, m. p. 238—239°, from acetic acid (Found: C, 79·1; H, 3·6. Calc. for $C_{18}H_{10}O_3$: C, 78·8; H, 3·7%). Koelsch and Rosenwald (*J. Amer. Chem. Soc.*, 1937, **59**, 2166) report m. p. 239—240°.

One of us (G. M. B.) has been working with an I.C.I. Research Fellowship, and we also thank the D.S.I.R. for a Maintenance Allowance (to J. E. C.). Microanalyses have been carried out by Mr. J. M. L. Cameron and Miss R. H. Kennaway.

UNIVERSITY OF GLASGOW. [*Received, October 13th,* 1948.]