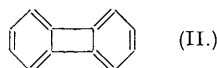
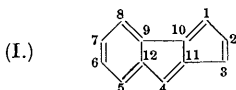


187. Attempts to prepare New Aromatic Systems. Part I. cyclopentindene. Phenylcyclopentanecarboxylic Acids, and Derived Ketones.

By WILSON BAKER and W. G. LEEDS.

This paper describes the synthesis of 4-keto-1 : 2 : 3 : 4 : 10 : 11-hexahydrocyclopentindene (III), which is a possible intermediate in the preparation of the unknown aromatic compound cyclopentindene. Benzene and cyclopent-1-enecarboxylic acid react in the presence of aluminium chloride to give a mixture of 2- and 3-phenylcyclopentane-1-carboxylic acids (IV) and (VI), and 4-keto-1 : 3-endoethylene-1 : 2 : 3 : 4-tetrahydronaphthalene (VII). The structures of the two acids have been established, and derivatives are described. The acids are readily cyclised to the ketones (III) and (VII) respectively, the latter being a derivative of benzocycloheptane. The confused literature concerning the phenylcyclopentanecarboxylic acids, their functional derivatives, and related ketones is surveyed and corrected. 2-Benzylcyclopentanone (XIV) and indan-3-one-1-carboxylic acid (XV), which are possible intermediates in the synthesis of cyclopentindene, have been prepared by improved methods.

PRELIMINARY experiments are now described directed towards the synthesis of the unknown aromatic hydrocarbon cyclopentindene (I), which is isomeric with diphenylene (II) (Lothrop, *J. Amer. Chem. Soc.*, 1941, **63**, 1187). This work was begun at a time when it seemed possible that diphenylene might really be cyclopentindene, but conclusive evidence that diphenylene is (II) has since been afforded by (a) electron diffraction studies (Waser and Schomaker, *J. Amer. Chem. Soc.*, 1943, **65**, 1451), (b) ready catalytic reduction to diphenyl (Baker, *J.*, 1945, 265), (c) X-ray crystallographical analysis (Waser and Chia-Si Lu, *J. Amer. Chem. Soc.*, 1944, **66**, 2035). The name cyclopentindene was suggested for (I) by Patterson and Capell ("The Ring Index", 1940, p. 204), and (I) may also be termed "benzopentalene", "pentalene" (*idem, ibid.*, p. 110) being the unknown hydrocarbon, C₈H₆, consisting of two fused cyclopentadiene rings.

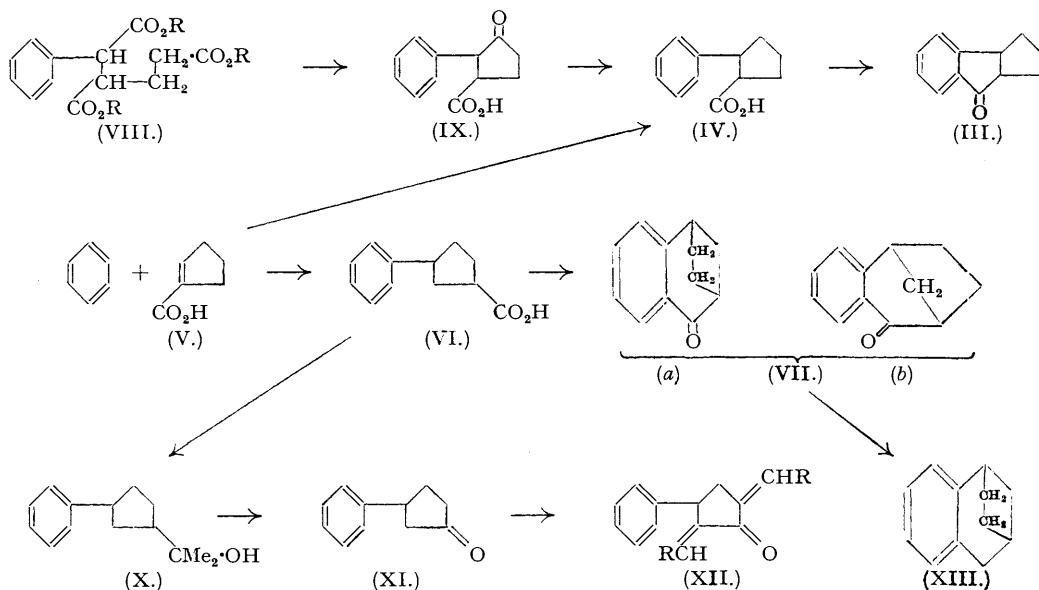


Pentalene was first postulated as a possible aromatic compound by Armit and Robinson (*J.*, 1922, **121**, 828), and unsuccessful attempts were made to prepare it by dehydrogenation of its octahydro-derivative (Barrett and Linstead, *J.*, 1936, 612; see also Baker, *loc. cit.*). The only known derivatives of pentalene are the complex diphenyl and dichloro-derivatives of 1 : 2 : 4 : 5-dibenzpentalene (2 : 3-benzocyclopentindene) (Brand, *Ber.*, 1912, **45**, 3071; Brand and Ludwig, *ibid.*, 1920, **53**, 809; Brand and Hoffmann, *ibid.*, p. 815; Brand and Müller, *ibid.*, 1922, **55**, 601; Brand, Gabel and Ott, *ibid.*, 1936, **69**, 2504; Wawzonek, *J. Amer. Chem. Soc.*, 1940, **62**, 745) which have been termed diphenusuccindadienes.

The present work had as its object the synthesis of compounds containing the hexahydrocyclopentindene system which, by direct or indirect processes of dehydrogenation, might be converted into the fully aromatic type. Of the various routes which were considered, the most direct appeared to be the preparation of 4-keto-1 : 2 : 3 : 4 : 10 : 11-hexahydrocyclopentindene (III) by the cyclisation of 2-phenylcyclopentane-1-carboxylic acid (IV). The synthesis of this acid, however, has not proved straightforward, and the work has disclosed a number of inaccuracies and misinterpretations in the literature.

A direct synthesis of the acid (IV) appeared to be offered by the addition of benzene to cyclopent-1-enecarboxylic acid (V). This reaction has been investigated by Nenitzescu and Gavát (*Annalen*, 1935, **519**, 260) who reported that, in presence of aluminium chloride, migration of the double bond occurred, giving a liquid 3-phenylcyclopentane-1-carboxylic acid (VI), the structure of which was proved by independent synthesis from 1 : 4-dibromo-2-phenylbutane and malonic ester, followed by hydrolysis and decarboxylation. Reinvestigation of this reaction showed, however, that under mild conditions it gives mainly 3-phenylcyclopentanecarboxylic acid (VI), but at the boiling point of benzene it yields a liquid mixture of 3-phenylcyclopentanecarboxylic acid (VI), 2-phenylcyclopentanecarboxylic acid (IV), 4-keto-1 : 3-endoethylene-1 : 2 : 3 : 4-tetrahydronaphthalene (VII), and a hydrocarbon, probably phenylcyclopentane. Some specimens of the mixed acids prepared by the latter procedure partially crystallised at 0°, and a solid acid, m. p. 87—88°, was isolated in up to 10% of the total weight of acids. The solid and liquid acids gave very sparingly soluble S-benzylthiuronium salts, and by repeated crystallisation of the latter salt the free originally liquid acid has been obtained also in the crystalline state, and has m. p. 17—18.5°. The higher- and lower-melting acids were

characterised as 2-phenylcyclopentanecarboxylic acid (IV) and 3-phenylcyclopentanecarboxylic acid (VI) respectively as described in the following paragraphs. Both acids differ from the known racemic 1-phenylcyclopentane-1-carboxylic acid (Case, *J. Amer. Chem. Soc.*, 1934, 56, 716) which has m. p. 158—159°.



2-Phenylcyclopentane-1-carboxylic Acid, m. p. 87—88°.—Chatterjee (*J. Indian Chem. Soc.*, 1938, 15, 211) claims to have prepared this acid by an unambiguous but lengthy method and described it as an oil. In view of the great ease of crystallisation of the acid, m. p. 87—88°, it did not seem likely that the two could be identical, but they have, in fact, proved to be so. Repetition of Chatterjee's synthesis, with modifications at intermediate stages but the same final stage, has yielded a crystalline acid, identical with that prepared by the addition of benzene to cyclopent-1-ene-carboxylic acid. Chatterjee's method consisted in condensing benzaldehyde cyanohydrin with the sodio-derivative of cyanoacetic ester and then with ethyl β -chloropropionate to give ethyl $\gamma\delta$ -dicyano- γ -carbethoxy- δ -phenyl-*n*-valerate, Ph-CH(CN) \cdot C(CN)(CO₂Et) \cdot CH₂ \cdot CH₂ \cdot CO₂Et, hydrolysing and re-esterifying to give ethyl $\gamma\delta$ -dicarboethoxy- δ -phenyl-*n*-valerate (VIII; R = Et), cyclising with sodium to ethyl 2-phenylcyclopentan-3-one-1:4-dicarboxylate, hydrolysing to 2-phenylcyclopentan-3-one-1-carboxylic acid (IX), and finally reducing by Clemmensen's method to 2-phenylcyclopentane-1-carboxylic acid (IV). As both (IV) and (IX) were required in some quantity for later work, a detailed study has been made of Chatterjee's series of reactions and considerable improvements effected. The dicyano-intermediate, ethyl $\gamma\delta$ -dicyano- γ -carbethoxy- δ -phenyl-*n*-valerate, is best prepared by condensation of ethyl β -chloropropionate with the sodio-derivative of ethyl $\alpha\beta$ -dicyano- β -phenylpropionate, itself formed by the direct addition of sodium cyanide to ethyl benzylidene-cyanoacetate. Neither the ethyl benzylidene-cyanoacetate nor the ethyl $\alpha\beta$ -dicyano- β -phenylpropionate need necessarily be isolated. Hydrolysis and esterification with methyl alcohol gave the methyl ester (VIII; R = Me), and this underwent smooth cyclisation in presence of methyl-alcoholic sodium methoxide to the 2-phenylcyclopentanone derivative.

cis- and *trans*-Forms of 2-phenylcyclopentane-1-carboxylic acid are possible, and it is not known with certainty which structure represents the acid, m. p. 87—88°. In view, however, of the fact that the acid is readily cyclised to a ketone (see below), it may be assumed provisionally that it is the *cis*-form.

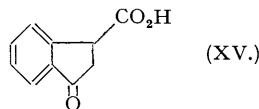
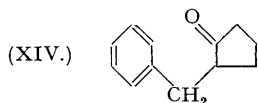
3-Phenylcyclopentane-1-carboxylic Acid, m. p. 17—18.5°.—There could be little doubt that this acid, although previously described as a liquid, was identical with the 3-phenylcyclopentane-1-carboxylic acid of Nenitzescu and Gavât (*loc. cit.*). As, however, a direct comparison of specimens was not possible, the acid was submitted to the Barbier-Wieland degradation, giving, *via* its methyl ester and 3-phenylcyclopentylidimethylcarbinol (X), 3-phenylcyclopentanone (XI), the position of the carbonyl group, and hence that of the original carboxyl group, being

established by the preparation of a dibenzylidene derivative (XII; R = Ph), and a *dipiperonylidene* derivative (XII; R = 3 : 4-methylenedioxyphenyl). The easy cyclisation of the acid (VI) to a ketone (see below) strongly suggests that it is the *cis*-isomeride.

Cyclisation of the phenylcyclopentanecarboxylic acids (IV) and (VI) is effected smoothly in 85% yield by heating with a mixture of syrupy phosphoric acid and phosphoric anhydride, and gives the liquid ketones, 4-keto-1 : 2 : 3 : 4 : 10 : 11-hexahydrocyclopentindene (III) and 4-keto-1 : 3-endoethylene-1 : 2 : 3 : 4-tetrahydronaphthalene (VIIa); the latter may equally be regarded as the bridged benzendomethylenecycloheptenone derivative (VIIb). The previously mentioned formation of a small amount of the ketone (VII) by the interaction of benzene, cyclopent-1-ene-carboxylic acid (V), and aluminium chloride, is explained by the fact that 3-phenylcyclopentane-1-carboxylic acid (VI) undergoes partial cyclisation to (VII) under the influence of aluminium chloride in boiling benzene. Yields of 20—40% of the ketone (VII) from the acid (VI) have been obtained by the action of phosphorus oxychloride, 80% sulphuric acid, or phosphoric anhydride in toluene, and by the action of stannic chloride on the acid chloride in benzene solution. The easy formation of (VII) opens up the possibility of a new route to the difficultly accessible benzocycloheptenone series. The ketones were characterised as 2 : 4-dinitrophenylhydrazones and as semicarbazones. The semicarbazone of (VII) forms well-developed crystals containing half a molecule of solvent of crystallisation from methyl and ethyl alcohols and from toluene. The toluene is readily detected by a micro-modification of Ramsden's test (see experimental section). In addition to the unexplained fact that Chatterjee's 2-phenylcyclopentane-1-carboxylic acid was an oil, is his curious claim that the related ketone, prepared by cyclisation of the acid chloride with aluminium chloride, gives a semicarbazone, m. p. 170°. We find, however, that the semicarbazone of the ketone (III) melts at 242° and does not contain solvent of crystallisation.

Mention must also be made of the work of von Braun and Kühn (*Ber.*, 1927, 60, 2557) who described as 2-phenylcyclopentane-1-carboxylic acid a product prepared by the addition of hydrogen bromide to 1-phenylcyclopent-2-ene, and conversion of the resulting phenylbromocyclopentane into a carboxylic acid *via* the derived Grignard reagent. This acid was an oil, possibly not homogeneous, from which an impure anilide, m. p. 93—95°, was obtained, thus excluding the possibility that their acid was identical with the 2-phenylcyclopentane-1-carboxylic acid described in this paper, the anilide of which melts at 90—91°. Von Braun and Kühn were able to cyclise their acid to a ketone by treatment of its chloride with aluminium chloride, and dismissed the possibility that the acid might be 3-phenylcyclopentane-1-carboxylic acid on the unjustified assumption that such an acid could not undergo ring closure to a cyclic ketone. It is most probable that the acid described by von Braun and Kühn was at least mainly 3-phenylcyclopentane-1-carboxylic acid (VI); this view is consistent with the melting point of their crude anilide, and with the fact that the related ketone gave a semicarbazone, m. p. 170°, from methyl alcohol [the semicarbazone of (VII) has initial m. p. ca. 170° when crystallised from methyl or ethyl alcohols—see experimental section], although no mention is made of solvent of crystallisation.

Reduction of (VII) by Clemmensen's method yields the liquid 1 : 3-endoethylene-1 : 2 : 3 : 4-tetrahydronaphthalene (XIII), which gives a well-crystalline, but incompletely homogeneous *sulphonamido*-derivative. This is probably a mixture of the 6- and 7-sulphonamido-compounds.



A number of substances have been prepared as possible intermediates in the synthesis of compounds containing the cyclopentindene skeleton. (a) 2-Benzylcyclopentanone (XIV) has been prepared as follows. Ethyl 1-benzylcyclopentan-2-one-1-carboxylate is readily prepared by the condensation of benzyl chloride with ethyl cyclopentan-2-one-1-carboxylate in benzene solution in presence of sodium (with alcoholic sodium ethoxide the same reactants yield diethyl α -benzyladipate; Duff and Ingold, *J.*, 1934, 87), and hydrolysis with hydrochloric acid then yields 2-benzylcyclopentanone. This synthesis of 2-benzylcyclopentanone is more direct than that of Duff and Ingold (*loc. cit.*), who hydrolysed diethyl α -benzyladipate, and converted it into the ketone *via* the anhydride. (b) 2-Acetyl-1 : 3-diketointhane is produced in small yield by the condensation of monochloroacetone with 1 : 3-diketointhane in presence of alcoholic sodium ethoxide. (c) Indan-3-one-1-carboxylic acid (XV) is available in 61% yield from phenylsuccinic acid by reaction with thionyl chloride followed by treatment with aluminium

chloride in nitrobenzene. Cyclisation of phenylsuccinic acid was achieved in 22% yield by Speight, Stevenson, and Thorpe (*J.*, 1924, 125, 2190) by the use of concentrated sulphuric acid. The related *ethyl ester* and *amide* are described, and a *compound*, probably either ethyl 2-acetylidan-3-one-1-carboxylate or ethyl β -keto- β -(3-keto-1-indanyl)propionate, prepared from the former by reaction with ethyl acetate in presence of sodium ethoxide.

EXPERIMENTAL.

Reaction of Benzene with cyclopent-1-enecarboxylic Acid.—*cyclopent-1-enecarboxylic acid* was prepared according to Cook and Linstead (*J.*, 1934, 958), but difficulty was experienced with emulsions in extracting the corresponding nitrile prepared by the dehydration of *cyclopentanone cyanohydrin*. This difficulty is avoided and the yield of pure nitrile increased by first steam-distilling the reaction product, extracting it with benzene, and then distilling it in a vacuum. A solution of *cyclopent-1-enecarboxylic acid* (35 g., 1 mol.) in benzene (700 c.c.) was placed in a 3-l. three-necked flask fitted with reflux condenser and mercury-sealed stirrer. Powdered anhydrous aluminium chloride (135 g.; 3 mols., optimum quantity) was added during 30 minutes while cooling in ice. Stirring was continued for 1 hour at room temperature and for a further hour at 50°. After 20 hours at room temperature the product was poured on crushed ice and concentrated hydrochloric acid, most of the benzene removed in steam, and the liquid shaken with ether. The ethereal extract was shaken with excess of 15% aqueous sodium hydroxide, the ether layer separated, the alkaline layer acidified, and the oily product again extracted with ether, the extracts dried and distilled, giving slightly crude 3-phenylcyclopentane-1-carboxylic acid (VI) as a viscous oil, b. p. 154—156°/0.9 mm. (50.6 g.; 85% yield) (Found: equiv., 191. Calc. for $C_{12}H_{14}O_2$: equiv., 190). When less than 2.5 mols. of aluminium chloride are used, unchanged *cyclopent-1-enecarboxylic acid* is found in the reaction product.

When the reaction was carried out at the b. p. of the benzene, the yield of acidic product was somewhat diminished, and, in addition, there was isolated non-acidic material (2.2 g., b. p. 100—200°/20 mm.) which proved to be a mixture containing 4-*keto-1:3-endoethylene-1:2:3:4-tetrahydronaphthalene* (VII) and a hydrocarbon, probably phenylcyclopentane. These were separated by refluxing the mixture in alcoholic solution for 3 hours with excess of Girard T reagent and acetic acid, pouring the resulting mixture into dilute sodium carbonate solution at 0°, extracting the hydrocarbon with ether, and regenerating the ketone by hydrolysis with hydrochloric acid for 2 hours on the water-bath. The hydrocarbon was freed from the last traces of ketone by a further similar treatment with Girard T reagent, and was obtained after fractionation as an oil, b. p. 115°/19 mm. (lit., b. p. 116—117°/37 mm.) (Found: C, 90.0; H, 10.3. Calc. for $C_{11}H_{14}$: C, 90.3; H, 9.7%). The regenerated ketone (b. p. 166—169°/21 mm.; n_D^{20} 1.578) gave a 2:4-*dinitrophenylhydrazone*, crystallising from acetic acid in red needles, m. p. 240—242°, and 242—244° when mixed with the 2:4-dinitrophenylhydrazone of the ketone prepared by cyclisation of 3-phenylcyclopentane-1-carboxylic acid (VI) (see below).

2-Phenylcyclopentane-1-carboxylic Acid (IV).—Several samples of the acid which had been prepared at the b. p. of the benzene partially crystallised when kept at 0°. The separated 2-phenylcyclopentane-1-carboxylic acid crystallised from light petroleum (b. p. 60—80°) in boat-shaped plates, m. p. 87—88° (yield up to 10% of the weight of the mixed acids) (Found: C, 75.5; H, 7.4. Calc. for $C_{12}H_{14}O_2$: C, 75.8; H, 7.4%). The acid (IV) (1 g.) was exactly neutralised by *N*-sodium carbonate, and a solution of *S*-benzylthiuronium chloride (1 g.) in water (30 c.c.) added. The precipitated *S*-benzylthiuronium salt was collected, washed with water, dried, and crystallised rapidly twice from alcohol, being obtained in thin plates, m. p. 165° (fairly rapid heating) (Found: N, 7.8. $C_{12}H_{14}O_2, C_8H_{10}N_2S$ requires N, 7.9%).

3-Phenylcyclopentane-1-carboxylic Acid (VI).—The liquid acid (20 g.) which either failed to solidify or remained after the separation of the solid acid was converted into its *S*-benzylthiuronium salt in the manner described above. After crystallising rapidly first from 50% alcohol (1 litre) and then three times from alcohol it formed elongated plates, m. p. 169° (fairly rapid heating; conditions the same as above), depressed to 150° on admixture with the isomeric salt (Found: N, 7.8. $C_{12}H_{14}O_2, C_8H_{10}N_2S$ requires N, 7.9%). The 3-phenylcyclopentane-1-carboxylic acid (VI), after regeneration from this purified salt, distilled at 137—138°/0.2 mm. (d_{18}^{18} 1.108; n_D^{20} 1.5423), and crystallised on cooling to a solid, m. p. 17—18.5° (Found: C, 75.7; H, 7.4. Calc. for $C_{12}H_{14}O_2$: C, 75.8; H, 7.4%). The solubility of the acid (IV) in the pure acid (VI) at 15° is ca. 30 parts of (IV) to 100 parts of (VI).

Amide and Anilide of 3-Phenylcyclopentane-1-carboxylic Acid (VI).—The acid (6.8 g.) and thionyl chloride (6 c.c.) were heated for 1 hour at 70—75°; distillation then gave the acid *chloride* (6.6 g.) as a pungent, faintly yellow oil, b. p. 163°/20 mm. (Found: Cl, 17.3. $C_{12}H_{13}OCl$ requires Cl, 17.0%), converted by shaking with concentrated aqueous ammonia into the amide, which crystallised from ethylene chloride or water in very thin, almost rectangular, nacreous plates, m. p. 147—148° (Found: C, 75.8; H, 7.9; N, 7.5. Calc. for $C_{12}H_{15}ON$: C, 76.2; H, 8.0; N, 7.4%). The anilide, obtained by treating the acid chloride in dry ether with excess of aniline for 1 hour, is difficult to purify; it was crystallised twice from carbon tetrachloride—light petroleum (b. p. 40—60°), and finally from benzene—light petroleum (b. p. 60—80°) and obtained in minute plates, m. p. 106—107° (Found: C, 81.8; H, 7.5; N, 5.5. Calc. for $C_{18}H_{19}ON$: C, 81.5; H, 7.2; N, 5.3%).

Amide and Anilide of 2-Phenylcyclopentane-1-carboxylic Acid (IV).—These derivatives were prepared and crystallised in the same way as the corresponding isomerides. *2-Phenylcyclopentane-1-carboxamide* formed long needles, m. p. 146—147° (Found: C, 76.1; H, 7.9; N, 7.6. $C_{12}H_{15}ON$ requires C, 76.2; H, 8.0; N, 7.4%); the mixed m. p. with the 3-phenyl isomeride was ca. 115—125°. *2-Phenylcyclopentane-1-carboxyanilide* formed fine prisms, m. p. 90—91° (Found: C, 81.7; H, 7.2; N, 5.7. $C_{18}H_{19}ON$ requires C, 81.5; H, 7.2; N, 5.3%).

Ethyl $\alpha\beta$ -Dicyano- β -phenylpropionate.—To benzaldehyde (53 g.; 1 mol.) and cyanoacetic ester (56.5 g.; 1 mol.) in alcohol (100 c.c.) was added piperidine (2 c.c.), and the mixture rapidly warmed so

that the maximum temperature attained was 60°, left for 1 hour, and finally shaken under the tap (the condensation is exothermic); benzylidenecyanoacetic ester then crystallised. Powdered sodium cyanide (35 g.) was added and the mixture heated for 5 minutes on the water-bath, by which time the marked yellow colour had faded. The cooled mixture was treated with a solution of sodium hydroxide (20 g.) in water (500 c.c.), extracted with ether (250 c.c.), the aqueous layer acidified with concentrated hydrochloric acid (100 c.c.), and while warm a rapid current of air blown through it to remove ether and hydrogen cyanide. The solid product (seeding was sometimes required) was collected after cooling in ice, washed, and dried at a moderate temperature (yield 100 g.). The compound is difficult to crystallise, but the following method succeeds well. The crude material (100 g.) was dissolved in warm methyl alcohol (640 c.c.), and, after addition of water (300 c.c.), treated with charcoal and filtered. To the filtrate was added a little methyl alcohol to give a solution just clear at 30°. The solution was then seeded, cooled while shaking, and finally placed in the ice-chest. The solid was collected, washed with ice-cold 50% methyl alcohol (100 c.c.), and dried (yield 80.3 g.; m. p. 63—65°). The pure compound has m. p. 65° (cf. Baker and Lapworth, *J.*, 1925, **127**, 563).

γ -*Dicarboxy- δ -phenyl-n-valeric Acid* (VIII; R = H).—(a) From ethyl $\alpha\beta$ -dicyano- β -phenylpropionate. To a cooled solution of sodium (9.2 g.) in absolute alcohol (400 c.c.) was added ethyl $\alpha\beta$ -dicyano- β -phenylpropionate (91.2 g.; 1 mol.) and β -chloropropionic ester (60 g.; 1.1 mol.), and the mixture refluxed for 6 hours, after which the solvents were removed under diminished pressure. The remaining oily product was hydrolysed by refluxing it for 18 hours with concentrated hydrochloric acid (500 c.c.) and water (100 c.c.). Boiling water (400 c.c.) and charcoal (5 g.) were added, the liquid filtered (sintered glass) hot, and the charcoal washed with boiling water (100 c.c.). After thorough cooling the acid was collected, washed, and dried; yield 91.5 g.; m. p. 178—180°.

(b) A mixture of benzaldehyde (53 g.), cyanoacetic ester (56.5 g.), alcohol (200 c.c.), and piperidine (2 c.c.) was warmed to 60°; after 1 hour powdered sodium cyanide (25 g.; 1 mol.) was added and the mixture shaken whilst being heated on the water-bath for 5 minutes. After addition of ethyl- β -chloropropionate (68 g.; 1 mol.) and refluxing for 8 hours the liquid was filtered from sodium chloride, the solvents removed, and the product hydrolysed as before, concentrated hydrochloric acid (600 c.c.) and water (300 c.c.) being used. The yield of faintly coloured acid was 77.5 g., m. p. 175—177°. Method (a) yields 80 g. of the acid from 53 g. of benzaldehyde.

The trimethyl ester (VIII; R = Me) was prepared by refluxing the acid (70 g.) with absolute methyl alcohol (400 c.c.) containing hydrogen chloride (16 g.) for 18 hours, removing the alcohol and water under diminished pressure, distilling twice with benzene (100 c.c.), and refluxing as before with methyl-alcoholic hydrogen chloride (200 c.c.). After working up in the usual way the ester was obtained as a colourless oil, b. p. 182°/0.15 mm. (yield 69.6 g.) (Found: C, 62.1; H, 6.6. $C_{16}H_{20}O_6$ requires C, 62.3; H, 6.6%). This ester slowly crystallised, giving after several days a solid mass, m. p. 50—56°. It was recrystallised from a large volume of light petroleum (b. p. 60—80°), giving small, flat prisms, m. p. 84—88° (Found: C, 62.4; H, 6.6%), undoubtedly a mixture of stereoisomers.

2-Phenylcyclopentan-3-one-1-carboxylic Acid (IX) and *Enolic Form of Dimethyl 2-Phenylcyclopentanone-3:5-dicarboxylate*.—The preceding trimethyl ester (61.6 g.) was added to a solution of anhydrous sodium methoxide (21.6 g.) in absolute methyl alcohol (160 c.c.), and the mixture refluxed for 3½ hours. The methyl alcohol was now removed under diminished pressure and the residual oil (*) hydrolysed by refluxing it for 16 hours with concentrated hydrochloric acid (500 c.c.) and water (250 c.c.). A little charcoal was then added, and the boiling mixture filtered rapidly through a sintered glass funnel. The 2-phenylcyclopentan-3-one-1-carboxylic acid (IX) separated in fine prisms, m. p. 115° with some previous softening (Chatterjee, *loc. cit.*, gives m. p. 114—115°) (yield 37 g.).

When the cyclisation product obtained in the preceding reaction (*) was shaken in ethereal solution with aqueous sodium hydrogen carbonate, there was extracted a weakly acidic product (5—10 g.) which crystallised from dilute alcohol in flat, almost rectangular plates, m. p. 152° (Found: C, 65.0; H, 5.6. $C_{15}H_{16}O_5$ requires C, 65.1; H, 5.8%). This compound gives a powerful violet ferric chloride reaction in dilute alcohol, and is probably an *enolic form* of dimethyl 2-phenylcyclopentanone 3:5-dicarboxylate. The intensity of the ferric chloride reaction suggests that it is the hydrogen atom attached to carbon atom 5 of the cyclopentanone nucleus which is involved in the enolisation. Hydrolysis with hydrochloric acid as described above gives 2-phenylcyclopentan-3-one-1-carboxylic acid.

Reduction of 2-Phenylcyclopentan-3-one-1-carboxylic Acid (IX) to *2-Phenylcyclopentane-1-carboxylic Acid* (IV).—As the Clemmensen reduction carried out by Chatterjee (*loc. cit.*) led to an impure liquid acid, the following details of our procedure are given.

The keto-acid (IX) (18.3 g.), amalgamated zinc (200 g.), water (200 c.c.), concentrated hydrochloric acid (200 c.c.), and toluene (100 c.c.) were refluxed for 40 hours, with the addition of hydrochloric acid (50 c.c.) after 20 and 30 hours. The diluted liquid was extracted with ether; the extracts yielded a non-acidic oil (0.7 g.) and a mainly solid acid which, after crystallisation from light petroleum (b. p. 60—80°), gave the acid (IV), m. p. 87—88° (8.8 g.) (Found: C, 75.5; H, 7.4), identical (mixed m. p.) with that previously prepared by the condensation of benzene with cyclopent-1-enecarboxylic acid.

3-Phenylcyclopentylidimethylcarbinol (X).—Methyl 3-phenylcyclopentane-1-carboxylate was prepared from the acid (VI) by the Fischer-Speier method as an oil, b. p. 159—160°/20 mm.; n_D^{20} 1.524. The ester (6.3 g.) in dry ether was added to the Grignard reagent prepared from magnesium (1.5 g.), methyl iodide (8.8 g.), and ether (50 c.c.), and after 12 hours the ether-soluble material was refluxed for ½ hour in aqueous-alcoholic sodium hydroxide to hydrolyse any unchanged ester, and the neutral *carbinol* isolated and distilled (4.6 g.); b. p. 176°/24 mm.; n_D^{20} 1.5348 (Found: C, 81.8; H, 9.6. $C_{14}H_{20}O$ requires C, 82.3; H, 9.8%).

3-Phenylcyclopentanone (XI) and *Derivatives*.—The carbinol (X) (3 g.) in acetic acid (15 c.c.) was treated at ca. 35° with a solution of chromic acid (1.5 g.) in water (3 c.c.) and acetic acid (15 c.c.). After 24 hours the green solution was diluted and extracted with ether, the extracts shaken with water and aqueous sodium carbonate, dried, and the solvent removed, leaving crude 3-phenylcyclopentanone as a pleasant-smelling oil. This was characterised, and the position of the carbonyl group established, by the

preparation of the dibenzylidene derivative (XII; R = Ph), m. p. 181° (Borsche and Menz, *Ber.*, 1908, 41, 204, record m. p. 181°), and the *dipiperonylidene* derivative (XII; R = 3 : 4-methylenedioxyphenyl). The latter separated when an alcoholic solution of the crude ketone was treated with excess of piperonal and a drop of concentrated aqueous potassium hydroxide. After two crystallisations from ethyl acetate it formed bright-yellow, square-ended needles, m. p. 220° (Found : C, 76.7; H, 4.9. C₂₇H₂₀O₅ requires C, 76.4; H, 4.8%).

4-*Keto*-1 : 3-endoethylene-1 : 2 : 3 : 4-tetrahydronaphthalene (VII).—The liquid 3-phenylcyclopentane-1-carboxylic acid (VI) (5 g.) was added to a cooled mixture of phosphoric acid (25 c.c.; *d* 1.75) and phosphoric anhydride (25 g.), well stirred, and then heated on the steam-bath for 3 hours, water added, and the crude ketone extracted with ether. The extracts from 9 such experiments were united, washed with 15% aqueous sodium hydroxide (yield of recovered distilled acid, 4.2 g.), then with water, dried, and distilled twice, giving 4-*keto*-1 : 3-endoethylene-1 : 2 : 3 : 4-tetrahydronaphthalene (VII) (30.7 g., yield 85% allowing for the recovered acid) as a colourless oil, b. p. 162—163°/23 mm.; *d*₄²⁵ 1.119; *n*_D²⁵ 1.577 (Found : C, 83.5; H, 7.4. C₁₂H₁₂O requires C, 83.7; H, 7.0%). The 2 : 4-dinitrophenylhydrazone was crystallised from dioxan and then from a mixture of chloroform and ethyl acetate, and obtained as dark red needles; m. p. 248—249° (Found : C, 61.1; H, 4.4; N, 16.2. C₁₈H₁₆O₄N₄ requires C, 61.4; H, 4.5; N, 15.9%). This derivative is most conveniently crystallised from glacial acetic acid, but the melting point is then slightly lower, 244—246°, owing to retention of a trace of acetic acid. The semicarbazone prepared from the ketone (VII) (1 g.), alcohol (4 c.c.), water (3 c.c.), semicarbazide hydrochloride (1 g.), and hydrated sodium acetate (1 g.) at 30° for 1 hour and left overnight, was collected and washed with 50% alcohol (yield 1.25 g.). It separates from methyl alcohol in thick prisms which melt at ca. 170—171° with loss of solvent, resolidify, and finally melt at 191° (Found in material dried at 80° in a vacuum : C, 66.3; H, 6.8; loss of methyl alcohol on heating to 160°, 5.4. C₁₃H₁₅ON₃·½MeOH requires C, 66.1; H, 6.6; MeOH, 6.5%). From ethyl alcohol, the stout rhombic prisms melt at ca. 167—169° with loss of solvent (Found : loss in weight at 160°, 7.8. C₁₃H₁₅ON₃·½EtOH requires loss, 9.1%). From toluene, the white elongated prisms partially melt at 120—130°, then resolidify, and melt again at 191° [Found in material heated at 145° in a vacuum for 1 hour : N, 18.3. C₁₃H₁₅ON₃ requires N, 18.3%. Loss of toluene between 100° and 145° (no loss below 100°) in a vacuum, 16.8. C₁₃H₁₅ON₃·½C₇H₈ requires loss, 16.7%]. The toluene of crystallisation is readily detected by a micro-modification of Ramsden's test for aromatic hydrocarbons (see Bradley, Robinson, and Schwarzenbach, *J.*, 1930, 812). A few mg. of the substance are gently heated in a small ignition tube loosely fitted with a cork carrying a thin glass rod, the end of which has been dipped in a solution of paraformaldehyde in concentrated sulphuric acid, reaching to within about ¼ inch of the bottom of the tube. The rapid appearance of a pinkish-brown colouration on the glass rod indicates the presence of the vapour of the aromatic hydrocarbon.

4-*Keto*-1 : 2 : 3 : 4 : 10 : 11-hexahydrocyclopentindene (III).—2-Phenylcyclopentane-1-carboxylic acid (IV) (3 g.; m. p. 86—87°) was cyclised as in the previous case. The ketone (2 g.) was isolated as an oil, b. p. 152°/17 mm.; *d*₁₈⁸ 1.101; *n*_D²⁰ 1.5742 (Found : C, 84.0; H, 7.1. C₁₂H₁₂O requires C, 83.7; H, 7.0%). The 2 : 4-dinitrophenylhydrazone, after two crystallisations from glacial acetic acid, formed dark-red needles, m. p. 216—217° (Found in material dried at 100° in a vacuum over potassium hydroxide : C, 61.2; H, 4.3; N, 15.9. C₁₈H₁₆O₄N₄ requires C, 61.4; H, 4.5; N, 15.9%). The semicarbazone, prepared as in the case of the isomeride (VII), was twice crystallised from a large volume of ethyl alcohol, and formed elongated, hexagonal plates, m. p. ca. 242° (decomp.; rapid heating) (Found : C, 68.3; H, 7.0; N, 18.5. C₁₃H₁₅ON₃ requires C, 68.1; H, 6.6; N, 18.3%).

1 : 3-endoEthylene-1 : 2 : 3 : 4-tetrahydronaphthalene (XIII).—The ketone (VII) (1 g.), amalgamated zinc (30 g.), and concentrated hydrochloric acid (50 c.c.) were refluxed for 3 hours, dilute hydrochloric acid (50 c.c.) added, and heating continued for a further 8 hours. The diluted mixture yielded to ether a volatile mobile oil (410 mg.), b. p. 115—130°/20 mm. Fractionation gave the hydrocarbon (XIII), b. p. 117°/25 mm. (Found : C, 91.1; H, 9.1. C₁₂H₁₄ requires C, 91.1; H, 8.9%).

A monosulphonamido-derivative of (XIII) was prepared as follows. Chlorosulphonic acid (5 c.c.) was added during 5 minutes to a stirred solution of the hydrocarbon (1 g.) in chloroform (10 c.c.) at 0°. Stirring was continued for 1 hour, ice added, and the dried chloroform layer distilled and the residue treated with powdered ammonium carbonate for ½ hour at 100°. The product, isolated by the addition of water and purified by solution in aqueous sodium hydroxide, separated from benzene in plates (430 mg.), m. p. 133—145°. Repeated crystallisation from benzene raised the m. p. to 151—156° (Found : C, 61.0; H, 6.3; N, 6.2; S, 13.6. C₁₂H₁₆O₂NS requires C, 60.8; H, 6.3; N, 5.9; S, 13.5%).

Ethyl 1-Benzylcyclopentan-2-one-1-carboxylate.—To sodium (7.6 g.) powdered under toluene was added a solution of ethyl cyclopentan-2-one-1-carboxylate (52 g.) in benzene (250 c.c.), and the formation of the sodio-derivative completed by heating on the steam-bath for 2½ hours. Benzyl chloride (60 c.c., 1.5 mols.) was then added; the mixture was heated on the steam-bath for 14 hours, and, after the addition of water, the benzene layer was separated, the aqueous layer extracted with ether, and the two organic layers united, dried (Na₂SO₄), and distilled. The ethyl 1-benzylcyclopentan-2-one-1-carboxylate was obtained as a colourless oil (60 g., 73% yield), b. p. 183—186°/20 mm. (Found : C, 73.2; H, 7.4. Calc. for C₁₅H₁₈O₃ : C, 73.2; H, 7.3%).

2-Benzylcyclopentan-1-one (XIV).—Ethyl 1-benzylcyclopentan-2-one-1-carboxylate (60 g.) and concentrated hydrochloric acid (200 c.c.) were refluxed for 18 hours, with the addition of a further quantity of acid (100 c.c.) after 7 hours. Dilution, extraction with ether, and distillation gave 2-benzylcyclopentanone (28 g.), b. p. 150—155°/18 mm., *n*_D¹⁷ 1.534, and a fraction, b. p. 155—190°/18 mm., consisting largely of unhydrolysed ester, which after hydrolysis as before yielded a further quantity of 2-benzylcyclopentan-1-one (6.8 g.), b. p. 153—154°/19 mm.; *n*_D¹⁷ 1.534; *d*₄²⁰ 1.038. The semicarbazone separated from methyl alcohol in plates, m. p. 198—200° (Duff and Ingold, *loc. cit.*, record the same m. p.).

1 : 3-Diketeto-2-acetonilindane.—A solution of 1 : 3-diketoidane (4.9 g.; Teeters and Shriner, *J. Amer. Chem. Soc.*, 1933, 55, 3026) in ethyl alcohol (20 c.c.), ethyl acetate (60 c.c.), and chloroacetone (3.1 g.) was added during 45 minutes to a stirred solution of sodium (0.8 g.) in alcohol (40 c.c.) at 0°. Five minutes

after the addition the product was filtered from sodium chloride, and the filtrate acidified with a few drops of acetic acid and evaporated to dryness under diminished pressure on the water-bath. The dark residue was triturated with ether (500 c.c.) in 10 portions, and the ethereal solutions filtered and distilled to a small volume (10 c.c.); on standing, a crystalline material separated. This was crystallised several times from light petroleum (b. p. 80—100°), giving finally colourless needles (120 mg.), m. p. 129—130° (Found: C, 71.1; H, 5.0. $C_{12}H_{10}O_3$ requires C, 71.3; H, 4.9%).

Indan-3-one-1-carboxylic Acid (XV).—Phenylsuccinic acid (40 g.; Baker and Lapworth, *Org. Synth.*, Coll. Vol. I, p. 451) and thionyl chloride (40 c.c.) were heated on the water-bath for $\frac{1}{2}$ hour. Dry nitrobenzene (80 c.c.) and anhydrous aluminium chloride (40 g.) were added, the mixture kept at 80° for $1\frac{1}{2}$ hours, then poured into water (1 l.) and boiled to expel all nitrobenzene, water (250 c.c.) being added during the distillation so that the final volume was 700 c.c. The boiling solution, after addition of charcoal (20 g.), was filtered and cooled rapidly with shaking. The colourless, crystalline acid was collected, washed, and dried on the steam-bath till the melt of the hydrated acid (m. p. 84°) solidified to the anhydrous acid, m. p. 120°. Yield, 16.0 g. From the filtrate two further crops of the acid were obtained (4.4 g. and 2.0 g.; total 22.4 g., 61%) (Found in material crystallised from benzene: C, 68.1; H, 4.8. Calc. for $C_{10}H_8O_3$: C, 68.1; H, 4.6%).

The ethyl ester, prepared in the usual way, formed an oil, b. p. 198°/37 mm., which solidified, and, after crystallisation from warm light petroleum (b. p. 40—60°), was obtained in thin, nacreous, rectangular plates, m. p. 49—50° (Found: C, 70.5; H, 6.0. $C_{12}H_{12}O_3$ requires C, 70.6; H, 5.9%). The *semicarbazone* of this ethyl ester formed small crystals from alcohol, m. p. 207—209° (decomp.) (Found: C, 59.9; H, 5.7. $C_{13}H_{15}O_3N_3$ requires C, 59.8; H, 5.8%).

Difficulty was experienced in preparing the amide from the foregoing ester owing to the formation of dark, intractable products. The ester (0.5 g.) was mixed with aqueous ammonia (10 c.c.; d 0.88) and just enough alcohol to give a homogeneous solution. After standing overnight the dark brown solution was evaporated to dryness, and the amide crystallised thrice from water (charcoal), giving colourless needles (0.1 g.), m. p. 177—178° (Found: C, 68.8; H, 5.4; N, 8.3. $C_{10}H_9O_2N$ requires C, 68.6; H, 5.1; N, 8.0%).

Condensation of Ethyl Indan-3-one-1-carboxylate with Ethyl Acetate.—To a solution of sodium (0.6 g.; 2 mols.) in ethyl alcohol was added ethyl acetate (30 c.c.), and then, in an atmosphere of nitrogen, a solution of ethyl indan-3-one-1-carboxylate (3 g.) in ethyl acetate (15 c.c.). The dark reddish-brown mixture was kept for 48 hours (in contact with air it became bright green). Excess of 2N-sodium hydroxide was added, and the mixture was extracted with ether, acidified, and the reddish product taken up in ether and shaken with aqueous sodium hydrogen carbonate. The ether yielded an oil which partly crystallised on treatment with methyl alcohol, and, after being pressed on porous porcelain, was finally obtained from light petroleum (b. p. 60—80°) (charcoal) as faintly purple, hexagonal plates (0.1 g.), m. p. 85—86° (Found: C, 68.3; H, 5.6. $C_{14}H_{14}O_4$ requires C, 68.3; H, 5.7%). This compound, either ethyl 2-acetylindan-3-one-1-carboxylate, or ethyl β -keto- β -(3-keto-1-indanyl)propionate, gives a deep red colour with alcoholic ferric chloride.

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