

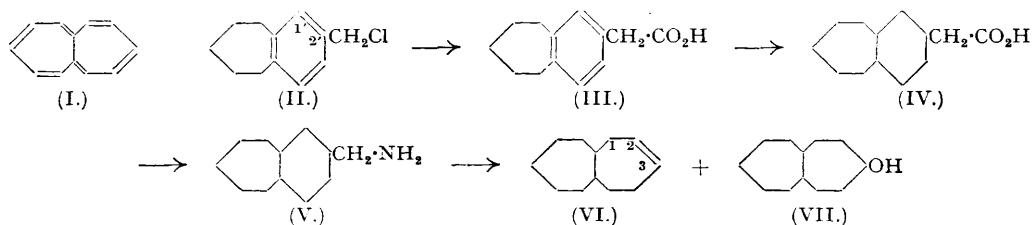
### 151. *Attempts to Prepare New Aromatic Systems. Part II.* *Heptalene.*

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Experiments were directed towards the synthesis of heptalene (I). Benzcycloheptene is converted through its 2'-chloromethyl derivative (II) into the fully saturated aminomethyl compound (V), which yields by the Demjanov reaction a 3-hydroxydodecahydroheptalene and a decahydroheptalene (VI). Attempts to effect catalytic dehydrogenation of (VI) have been unsuccessful.

In model experiments leading to the hydroazulene series ethyl  $\delta$ -2-ketocyclopentylvalerate (VIII) has been converted into the ketones (XI) and (XII).

THE possibility that a bicyclic, unsaturated hydrocarbon of aromatic type possessing two fused seven-membered rings might be prepared was first mentioned by Baker (*J.*, 1945, 264). This substance (I), for which the name heptalene has been used by one of us on numerous occasions since 1944, is a ring homologue of azulene, and the present experiments were begun with the object of attempting to prepare this hydrocarbon. Partly because collaboration between the authors is no longer possible, and partly because others have started work in this series (Horn and Rapson, *Nature*, 1947, **160**, 829; *J.*, 1949, 2421; see also Büchi and Jeger, *Helv. Chim. Acta*, 1949, **32**, 538, who have described the synthesis of certain derivatives of 5:5:0-bicyclododecane), it is thought desirable to publish our experiments so far as they have progressed. There is as yet no factual information as to the existence or non-existence of compounds of the "aromatic" heptalene type, although some calculations have been made in the attempt to assess the probable stability of such a conjugated system (Craig and Maccoll, *Nature*, 1948, **161**, 481; *J.*, 1949, 964).



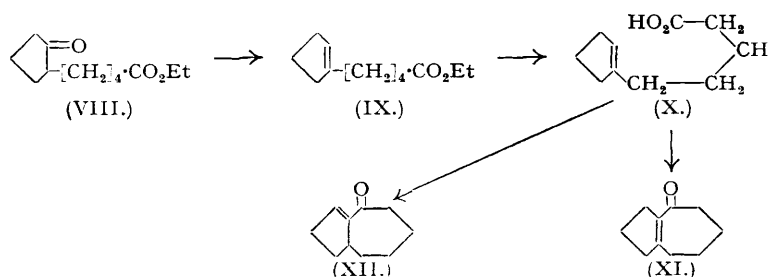
The present synthetical method starts from benzcycloheptene (benzsuberane) and uses the Demjanov reaction for the enlargement of the finally reduced six-membered ring; it is analogous to a synthesis of azulene from indane described by Arnold (*Ber.*, 1943, **76**, 777; cf. also Plattner, Fürst, and Studer, *Helv. Chim. Acta*, 1947, **30**, 1091). Chloromethylation of benzcycloheptene

yielded 2'-chloromethylbenzycycloheptene (II) which is orientated by analogy, and this was then converted into, successively, 2'-cyanomethylbenzycycloheptene and the homogeneous, crystalline benzycycloheptene-2'-acetic acid (III). The ethyl ester of (III) was reduced with hydrogen in presence of Adams's platinum oxide catalyst to ethyl cyclohexanocycloheptane-2'-acetate, hydrolysis of which yielded an almost homogeneous cyclohexanocycloheptane-2'-acetic acid (IV). Application of the von Auwers-Skita rule (von Auwers, *Annalen*, 1920, **420**, 84; Skita, *Ber.*, 1920, **53**, 1792) suggests that the acid (IV) probably possesses the *cis*-configuration of the two rings. Treatment of this acid with sodium azide under the conditions of the Schmidt reaction then gave 2'-aminomethylcyclohexanocycloheptane (V), characterised as the crystalline benzoyl derivative. The action of nitrous acid on (V) yielded an unsaturated hydrocarbon, probably the  $\Delta^2$ -decahydroheptalene (VI), and an alcohol, probably 3-hydroxy-dodecahydroheptalene (VII), which was not obtained pure.

A few attempts have been made to dehydrogenate decahydroheptalene (VI) over palladium-charcoal at 310–330°/14 mm.; the product, a colourless oil, possessed a higher refractive index than (VI) and was unsaturated, but did not yield a picrate. The lengthy synthetical processes involved in the preparation of the aminomethyl compound (V) have allowed the final reactions which might lead to the synthesis of heptalene to be performed only on a very small scale.

A second projected synthesis of heptalene involved the formation of a seven-membered ring by the cyclodehydration of a suitable unsaturated acid, as in (X). This method has now, however, been described by Büchi and Jeger (*loc. cit.*), who started from a cycloheptane derivative, but our preliminary experiments to test the feasibility of this approach started from a cyclopentane and led to the reduced azulene series.

Ethyl cyclopentanone-2-carboxylate was condensed with ethyl  $\delta$ -iodovalerate giving ethyl  $\delta$ -(2-keto-1-carbethoxycyclopentyl)valerate, which was simultaneously hydrolysed and decarboxylated, and then esterified, yielding ethyl  $\delta$ -2-ketocyclopentylvalerate (VIII). The ketone (VIII) was then reduced by the Meerwein-Ponndorf method to the secondary alcohol, and dehydrated with thionyl chloride to the unsaturated ester, probably mainly ethyl  $\delta$ -cyclo-



pent-1-enylvalerate (IX). Hydrolysis of (IX) yielded the corresponding acid (X) (uncharacterised), which was cyclised (a) by treatment of the acid chloride with stannic chloride in carbon disulphide (method due to Cook and Lawrence, *J.*, 1935, 1637), and (b) by treatment of the free acid with zinc chloride in acetic acid-acetic anhydride (method due to Bachmann and Dreiding, *J. Org. Chem.*, 1948, **13**, 324). Both cyclisation procedures yielded small quantities of liquid ketonic products giving deep-red 2:4-dinitrophenylhydrazones, C<sub>16</sub>H<sub>18</sub>O<sub>4</sub>N<sub>4</sub>, which although closely similar are not identical. The non-identity of these 2:4-dinitrophenylhydrazones, which give no depression of the melting point on admixture, was confirmed by the fact that their X-ray powder photographs, kindly taken by Dr. T. Malkin, were slightly but definitely different. The intense colour of these compounds shows that they are derived from the  $\alpha\beta$ -unsaturated ketones (XI) and (XII). Should the olefinic bond in (X) be in the alternative position cyclisation might theoretically give rise to a bicyclo[5:2:1]decenone with an eight-membered ring, but this is considered improbable. The liquid ketone (XI) was first prepared by Hückel and Schnitzpahn by internal condensation of 1:6-diketocyclodecane (*Annalen*, 1933, **505**, 274) and characterised by means of its crystalline oxime. We have been unable to obtain a solid oxime from either of our ketones, and it has thus been impossible to confirm the identity of their ketone previously described with either of ours.

During the course of this work we had occasion to make *trans*-cyclopentane-1:2-dicarboxylic acid. This acid has previously been made from trimethylene dibromide *via* trimethylenebis-malonic ester, cyclisation of the related disodio-derivative by treatment with bromine, and

finally hydrolysis and decarboxylation (Perkin, *J.*, 1887, **51**, 240; 1894, **65**, 584; Uschakov, *J. Russ. Phys. Chem. Soc.*, 1929, **61**, 795; Kon and Nandi, *J.*, 1933, 1628; Guha and Seshriengar, *Ber.*, 1936, **69**, 1212). We find that the acid is more conveniently prepared from the readily available ethyl cyclopent-1-enylcarboxylate (from cyclopentanone cyanohydrin by dehydration and simultaneous hydrolysis and esterification; Cook and Linstead, *J.*, 1934, 959), by addition of the elements of hydrogen cyanide to the double bond, and hydrolysis of the cyano-ester. The diamide and dinitrile of *trans*-cyclopentane-1:2-dicarboxylic acid are described.

## EXPERIMENTAL.

*Preparation of  $\delta$ -Phenylvaleric Acid from 3-Phenylpropyl Bromide.*—3-Phenylpropyl alcohol (136 g.) was refluxed for 4 hours with 48% hydrobromic acid (480 g.), the mixture cooled, diluted, and extracted with ether, and the extract washed with aqueous sodium carbonate, dried, and distilled, giving the bromide (170 g., 82%), b. p. 107–110°/8–9 mm. The procedure of Norris, Watt, and Thomas (*J. Amer. Chem. Soc.*, 1916, **38**, 1078) gives a 63% yield. Condensation of this bromide (80 g.) with ethyl malonate (von Braun and Kruber, *Ber.*, 1912, **45**, 386) gave ethyl 3-phenylpropylmalonate (70 g.; b. p. 180–195°/13 mm.), hydrolysis and decarboxylation of which gave finally  $\delta$ -phenylvaleric acid, which after recrystallisation from light petroleum (b. p. 60–80°) had m. p. 57° (lit., 61°) (yield 30 g.).

*Preparation of  $\delta$ -Phenylvaleric Acid from Cinnamylidenemalonate Ester.*—Cinnamaldehyde (82.5 g.), ethyl malonate (100 g.), benzene (200 c.c.), and piperidine (5 c.c.) were refluxed and slowly distilled till the calculated amount of water had collected (7½ hours). After cooling of the mixture, benzene (100 c.c.) was added and the solution washed successively with water, dilute hydrochloric acid, and sodium hydrogen carbonate solution, dried, and distilled, giving ethyl cinnamylidenemalonate, b. p. 188–190°/7 mm. (126 g.). Hydrolysis of this ester (172 g.) was effected by boiling aqueous sodium hydroxide (230 g. in 700 c.c.) (8–9 hours); water (500 c.c.) was then added, reduction carried out with Raney nickel alloy as described by Cook, Philip, and Somerville (*J.*, 1948, 164), and the resulting saturated acid decarboxylated, giving finally  $\delta$ -phenylvaleric acid which, after purification as before, was obtained in colourless crystals, m. p. 60° (70 g.).

*1:2-Benzocyclohepten-3-one.*—The following method is based on that of Plattner (*Helv. Chim. Acta*, 1944, **27**, 804); it is carried out much more rapidly in almost twice the concentration but gives the same yield of benzocycloheptenone.  $\delta$ -Phenylvaleryl chloride (19.5 g.) in carbon disulphide (300 c.c.) was added (4 hours) to a stirred refluxing mixture of aluminium chloride (27.5 g.) and carbon disulphide (200 c.c.), and stirring was continued for 6 hours, after which the solvent was removed by distillation and the residue poured on ice (500 g.) and steam-distilled. The benzocycloheptenone, isolated from the distillate by means of ether, was a liquid, b. p. 128–130°/6–7 mm. (14.0 g.).

*2'-Chloromethylbenzocycloheptene (II).*—Benzocycloheptene (56 g.), aqueous formaldehyde (35 c.c.; 40% solution), and concentrated hydrochloric acid (77 c.c.) were stirred vigorously at 60–70°, concentrated sulphuric acid (52 c.c.) was added dropwise during 7 hours, and stirring continued for a further 20 hours at the same temperature. The cooled mixture was then diluted with water and extracted with ether, and the extracts were washed with sodium hydrogen carbonate solution, dried, and distilled, giving two main fractions, (1) b. p. 60–120°/6 mm. (15 g.) consisting mainly of benzocycloheptene, and (2) b. p. 120–133°/6 mm. (46 g.). Redistillation of fraction (2) gave 2'-chloromethylbenzocycloheptene (II) (40 g.), b. p. 138–141°/9 mm.,  $n_D^{25}$  1.5672 (Found: C, 73.8; H, 7.6; Cl, 18.7.  $C_{12}H_{15}Cl$  requires C, 74.0; H, 7.7; Cl, 18.3%).

*2'-Cyanomethylbenzocycloheptene.*—To (II) (35 g.) in ethanol (200 c.c.) was added a solution of potassium cyanide (23 g.) in water (50 c.c.), and the mixture refluxed for 5 hours. Dilution with water and extraction with ether yielded 2'-cyanomethylbenzocycloheptene (28 g.) as a colourless oil, b. p. 155–170°/10 mm.,  $n_D^{25}$  1.5518 (Found: C, 84.0; H, 8.1; N, 7.6.  $C_{13}H_{15}N$  requires C, 84.3; H, 8.1; N, 7.6%).

*Benzocycloheptene-2'-acetic Acid (III).*—2'-Cyanomethylbenzocycloheptene (28 g.) was refluxed for 2 hours with water (25 c.c.), concentrated sulphuric acid (25 c.c.), and glacial acetic acid (25 c.c.). The mixture was diluted with water and extracted with ether, the extracts were shaken with dilute sodium hydroxide, the alkaline layer was acidified, and the precipitated benzocycloheptene-2'-acetic acid (III) crystallised from aqueous acetic acid and then twice from light petroleum (b. p. 60–80°), giving fine needles (10.3 g.), m. p. 127° (Found: C, 76.6; H, 7.7.  $C_{13}H_{15}O_2$  requires C, 76.5; H, 7.8%). The anilide was prepared by heating the acid (1 g.) with thionyl chloride (1 c.c.) under reflux till reaction was complete, diluting the mixture with ether, and adding aniline (1 g.) slowly with cooling; the ethereal solution, after being washed with dilute hydrochloric acid, yielded a solid which when crystallised three times from benzene-light petroleum (b. p. 60–80°) gave fine, silky needles, m. p. 142–143° (Found: C, 81.3; H, 7.4; N, 5.4.  $C_{18}H_{19}ON$  requires C, 81.5; H, 7.2; N, 5.3%).

*Ethyl Benzocycloheptene-2'-acetate.*—(a) The preceding acid (10 g.) was refluxed with ethanol (100 c.c.) and concentrated sulphuric acid (3 c.c.) for 4 hours and the ester isolated in the usual way as a colourless oil (10.4 g.), b. p. 151–154°/4 mm.,  $n_D^{25}$  1.5282 (Found: C, 77.5; H, 8.7.  $C_{15}H_{20}O_2$  requires C, 77.6; H, 8.6%).

(b) 2'-Cyanomethylbenzocycloheptene (28 g.) was refluxed for 18 hours with ethanol (105 c.c.) and concentrated sulphuric acid (10 c.c.), excess of ethanol removed under diminished pressure, water added, and the mixture extracted with ether. After being shaken with sodium hydrogen carbonate solution and drying, the ethereal layer yielded the ester (25 g.), b. p. 165–167°/9 mm.

Hydrolysis of the ester (25 g.) by boiling with potassium hydroxide (20 g.), water (20 c.c.), and ethanol (20 c.c.) for 4 hours yielded the free acid (III) which, after twice crystallising from dilute acetic acid and once from light petroleum (b. p. 60–80°), formed needles (13.2 g.), m. p. 127°.

*Ethyl cyclohexanocyclopentane-2'-acetate.*—Ethyl benzocycloheptene-2'-acetate (10.4 g.) in glacial acetic acid (100 c.c.) was shaken in hydrogen at atmospheric pressure in presence of Adams's platinum oxide catalyst (0.5 g.), rather more than the theoretical volume of hydrogen being absorbed in 72 hours.

After filtration the bulk of the solvent was removed under diminished pressure, the residue shaken with water and ether, and the ethereal layer shaken with sodium carbonate solution, dried, and distilled. *Ethyl cyclohexanocycloheptane-2'-acetate* was obtained as a colourless liquid (10.2 g.), b. p. 146—148°/4 mm.,  $n_D^{20}$  1.4826 (Found: C, 76.0; H, 10.8.  $C_{15}H_{26}O_2$  requires C, 75.6; H, 10.9%).

(*cis*-?)*cyclohexanocycloheptane-2'-acetic Acid* (IV).—The preceding ester (36 g.) was refluxed for 4 hours with potassium hydroxide (16 g.), water (40 c.c.), and ethanol (40 c.c.). After dilution, extraction with ether, and acidification, the semi-solid mass was collected and crystallised twice from light petroleum (b. p. 60—80°), giving *cyclohexanocycloheptane-2'-acetic acid* (IV) (11.5 g.) as small leaflets, m. p. 92—95° unaltered by further crystallisation (Found: C, 74.4; H, 10.6.  $C_{15}H_{22}O_2$  requires C, 74.3; H, 10.5%). The light petroleum mother-liquors yielded a further quantity of the acid, b. p. 169—171°/0.5 mm. (9.5 g.), which crystallised on storage.

*2'-Aminomethylcyclohexanocycloheptane* (V).—*cyclohexanocycloheptane-2'-acetic acid* (9.5 g.), dissolved in concentrated sulphuric acid (18 c.c.), was covered with a layer of chloroform (90 c.c.) and vigorously stirred while sodium azide (3.6 g.) was slowly added. Stirring was then continued whilst the temperature was raised to 45°, and after evolution of gas was complete the mixture was poured on ice, made alkaline with sodium hydroxide, and extracted with ether. The extract yielded *2'-aminomethylcyclohexanocycloheptane* (V) as an oil (7.1 g.), b. p. 108—110°/3 mm.,  $n_D^{20}$  1.5016 (Found: C, 79.7; H, 12.8; N, 7.6.  $C_{12}H_{22}N$  requires C, 79.6; H, 12.7; N, 7.7%). The *benzoyl* derivative, prepared by the Schotten-Baumann technique, was crystallised 3 times from aqueous ethanol and obtained as thin hexagonal plates, m. p. 129—131° (Found: C, 80.0; H, 9.7; N, 4.6.  $C_{19}H_{27}ON$  requires C, 80.0; H, 9.5; N, 4.6%).

*Action of Nitrous Acid on 2'-Aminomethylcyclohexanocycloheptane* (V). *Decahydroheptalene* (VI).—To the aminomethyl compound (V) (7.1 g.), dissolved in glacial acetic acid (3.5 c.c.) and water (70 c.c.), was added sodium nitrite (4.2 g.) in water (28 c.c.), and the mixture then heated on the water-bath until evolution of nitrogen had ceased. The oil which separated was extracted with ether, the extracts were washed with aqueous sodium hydroxide, dried, and distilled, giving two main fractions: (a) b. p. 53—93°/0.5 mm. (1.5 g.), and (b) b. p. 105—115°/1 mm.,  $n_D^{20}$  1.5022 (3.6 g.). Redistillation of fraction (a) over sodium gave *decahydroheptalene* (VI) as a colourless oil (1.0 g.), b. p. 58—62°/0.5 mm.,  $n_D^{20}$  1.5005, which became slightly brown when kept (Found: C, 87.2; H, 12.3.  $C_{12}H_{20}$  requires C, 87.8; H, 12.1%). Fraction (b) probably consists mainly of 3-hydroxydecahydroheptalene (VII) (Found: C, 77.8; H, 11.6.  $C_{12}H_{22}O$  requires C, 79.1; H, 12.1%).

*Ethyl 8-(2-Keto-1-carbethoxycyclopentyl)valerate*.—Ethyl 2-ketocyclopentane-1-carboxylate (24 g.) was added to powdered sodium (3.5 g.) and dry toluene (200 c.c.), and the mixture stirred till evolution of hydrogen had ceased (*ca.* 2 hours). Freshly distilled ethyl  $\delta$ -iodovalerate (39 g.; Carter, *J. Amer. Chem. Soc.*, 1928, **50**, 1967) was then added, and the mixture stirred and refluxed for 16 hours. Water was added, and the toluene layer separated, washed with dilute sodium hydroxide solution, dried, and distilled, yielding *ethyl 8-(2-keto-1-carbethoxycyclopentyl)valerate* as a colourless oil (28 g.), b. p. 180—182°/4 mm. (Found: C, 63.6; H, 8.7.  $C_{15}H_{24}O_5$  requires C, 63.4; H, 8.5%). This ester did not yield a crystalline 2 : 4-dinitrophenylhydrazone.

*Ethyl 8-2-Ketocyclopentylvalerate* (VIII).—The preceding ester (25 g.) was refluxed for 8 hours with concentrated hydrochloric acid (50 c.c.), diluted, and extracted with ether. The extract (A) was shaken with excess of dilute aqueous sodium hydroxide. The alkaline layer yielded to ether crude *8-2-ketocyclopentylvaleric acid* (7.6 g.) as an oil which failed to crystallise, but which readily gave a 2 : 4-dinitrophenylhydrazone which was crystallised 5 times from benzene-light petroleum (b. p. 60—80°) and obtained as orange plates, m. p. 145—146° (Found: C, 53.4; H, 5.8; N, 15.6.  $C_{16}H_{26}O_6N_4$  requires C, 52.7; H, 5.5; N, 15.4%). The crude acid (7.4 g.) was refluxed for 4 hours with ethanol (100 c.c.) and concentrated sulphuric acid, and the ester isolated in the usual way, combined with that remaining in the ethereal extract (A), and distilled, yielding *ethyl 8-2-ketocyclopentylvalerate* (VIII) (14.6 g.) as an oil, b. p. 124—125°/1.5 mm.,  $n_D^{20}$  1.4567 (Found: C, 67.2; H, 9.9.  $C_{12}H_{20}O_3$  requires C, 67.9; H, 9.4%). The 2 : 4-dinitrophenylhydrazone of this ester after crystallising twice from ethanol and once from methanol formed fine, orange-yellow plates, m. p. 78—79° (Found: C, 55.0; H, 6.1; N, 14.0.  $C_{18}H_{24}O_6N_4$  requires C, 55.1; H, 6.1; N, 14.3%).

*Ethyl 8-2-Hydroxycyclopentylvalerate*.—To a solution of aluminium isopropoxide, made from aluminium foil (3.1 g.) and isopropyl alcohol (34 c.c.) by refluxing with a trace of mercuric chloride and carbon tetrachloride for 6 hours, was added ethyl 8-2-ketocyclopentylvalerate (VIII) (8.1 g.) in isopropyl alcohol (50 c.c.). The mixture was refluxed and allowed to distil very slowly while isopropyl alcohol was added at the same rate; after 6 hours the distillate was free from acetone, and the solvents were then removed from the reaction mixture under diminished pressure. The product was then acidified with dilute hydrochloric acid and yielded to ether *ethyl 8-2-hydroxycyclopentylvalerate* as an oil (6.8 g.), b. p. 145—150°/4 mm. (Found: C, 69.1; H, 11.0.  $C_{15}H_{22}O_3$  requires C, 67.3; H, 10.3%). This ester is not entirely homogeneous and probably contains some of the related unsaturated ester (below), and there is also the possibility of some ester exchange with the isopropyl alcohol.

*Ethyl 8-cyclopent-1-enylvalerate* (IX).—The preceding hydroxy-ester (6.5 g.) in anhydrous ether (60 c.c.) containing pyridine (4.9 g.) was slowly treated with thionyl chloride (3.7 g.) at 0°, and 4 hours later water was added, and the ethereal layer was washed with dilute hydrochloric acid and then with sodium carbonate solution, dried, and distilled. The ester (IX) was obtained as a yellow oil (5.0 g.), b. p. 150—160°/5—6 mm.,  $n_D^{20}$  1.4572 (Found: C, 73.8; H, 10.7.  $C_{12}H_{20}O_2$  requires C, 73.5; H, 10.2%), which may contain some of the corresponding isopropyl ester. The free acid (X) obtained by hydrolysis with aqueous alcoholic potassium hydroxide was obtained as a pale yellow oil, b. p. 125—130°/1.6 mm.

*Cyclisation of 8-cyclopentylvaleric Acid* (X).—(a) (cf. Cook and Lawrence, *loc. cit.*). The crude acid (X) (1.5 g.) was converted into the chloride by the action of molecular quantities of thionyl chloride and pyridine in ether at 0°, filtration, and evaporation under diminished pressure. The chloride was treated in carbon disulphide solution with anhydrous stannic chloride in carbon disulphide at -10° and then allowed to reach room temperature overnight. After dilution the organic layer was washed with dilute sodium hydroxide solution and dried, the solvent removed under diminished pressure,



and the residual oil heated with dimethylaniline for 3 hours at 180°. Addition of excess of dilute hydrochloric acid and extraction with ether yielded a brown oil (0.9 g.), which yielded a 2:4-dinitrophenylhydrazone which, after two crystallisations from ethyl acetate, formed fine, deep-red needles, m. p. 242—243° (Found: C, 58.9; H, 5.7; N, 16.7.  $C_{16}H_{18}O_4N_4$  requires C, 58.2; H, 5.5; N, 17.0%). A crystalline oxime could not be obtained.

(b) (cf. Bachmann and Dreiding, *loc. cit.*). The crude acid (X) (2.9 g.) was dissolved in a solution of anhydrous zinc chloride (0.3 g.) in acetic acid (7 c.c.) and acetic anhydride (30 c.c.), and after 48 hours the mixture was heated to 70—80° for 1 hour and then well shaken with ether and dilute aqueous sodium hydroxide. The ethereal layer yielded a fraction (0.5 g.), b. p. 100—120°/2 mm., and a higher-boiling residue. The distillate gave a 2:4-dinitrophenylhydrazone which after 3 crystallisations from ethyl acetate formed fine, deep-red needles, m. p. 232° [the mixed m. p. with the 2:4-dinitrophenylhydrazone prepared by method (a) was 232°] (Found: C, 58.9; H, 5.6; N, 17.2%). Again, no crystalline oxime could be obtained.

*trans-cyclopentane-1:2-dicarboxylic Acid*.—Ethyl cyclopent-1-ene-1-carboxylate (67 g.; Cook and Linstead, *loc. cit.*) in ethanol (250 c.c.) was refluxed for 4 hours with aqueous potassium cyanide (34 g. in 70 c.c.), after which aqueous potassium hydroxide (30 g. in 60 c.c.) was added and refluxing continued for a further 6 hours. Concentrated hydrochloric acid (100 c.c.) was then added and cyclopent-1-ene-1-carboxylic acid removed in steam. When kept, the residual solution deposited *trans-cyclopentane-1:2-dicarboxylic acid* which was crystallised from water giving the colourless acid (33 g.), m. p. 160°.

The acid (10 g.) was heated with thionyl chloride (20 c.c.) for 1 hour and then distilled and the diacid chloride collected as an oil (10.5 g.), b. p. 98—100°/2 mm. This was added with shaking to aqueous ammonia (100 c.c.;  $d$  0.88) at 0°. The *diamide* separated from water in highly refracting, rectangular prisms (6.6 g.), m. p. 303° (Found: C, 53.5; H, 7.6; N, 18.0.  $C_7H_{12}O_2N_2$  requires C, 53.9; H, 7.7; N, 18.0%).

*trans-1:2-Dicyanocyclopentane*.—The preceding diamide (6.6 g.) was refluxed for 2 hours with thionyl chloride (20 c.c.), excess of the reagent removed by distillation, and the residue dissolved in ether, shaken with aqueous sodium carbonate, dried, and distilled. The *dinitrile* (3.6 g.) was collected at 122°/6 mm. as an oil which set to a glassy mass on cooling (Found: C, 69.7; H, 6.9.  $C_7H_8N_4$  requires C, 70.0; H, 6.7%).

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