

445. Internuclear Cyclisation. Part XIV.* Reactions with Hydroaromatic Rings.

By D. H. HEY and R. A. J. LONG.

Catalytic decomposition of the diazonium salts from ethyl *o*-amino- α -cyclohexenylcinnamate (I; R = Et, R' = H) and ethyl *o*-amino- α -2-methylcyclohexenylcinnamate (I; R = Et, R' = Me) (or the free acid) gave derivatives of tetrahydrophenanthrene, which were identified by conversion into phenanthrene and 1-methylphenanthrene respectively. These reactions provide the first examples of internuclear cyclisation of this type involving a hydroaromatic ring. Similar reactions with tetra- and hexa-hydrobenzoyl-*N*-methyl-*o*-phenylenediamine gave indeterminate results.

ALTHOUGH numerous reactions involving diazo-compounds have been recorded in which internuclear cyclisation has been effected with a variety of homocyclic and some heterocyclic aromatic compounds,^{1,2} no attempts appear to have been reported in which the cyclisation involves a non-aromatic ring. Such reactions would yield partially reduced systems, which are difficult of access by other methods, and might provide valuable evidence on the mechanism of the ring closure.

It has been shown by Schwenk and Papa³ that cyclohex-1-enylacetic acid and aromatic aldehydes give cyclohexenylcinnamic acids. By this method condensation with *o*-nitrobenzaldehyde in the presence of triethylamine gave α -cyclohex-1-enyl-*o*-nitrocinnamic acid, which was esterified and reduced to ethyl *o*-amino- α -cyclohex-1-enylcinnamate (I; R = Et, R' = H). The derived diazonium fluoroborate decomposed in acetone in the presence of copper powder to give ethyl 5 : 6 : 7 : 8-tetrahydrophenanthrene-9-carboxylate (II; R = Et, R' = H) in 50% yield. This ester was hydrolysed to the acid (m. p. 210°), which gave phenanthrene (III; R' = H) on dehydrogenation and decarboxylation. A similar result was obtained when the aqueous diazonium sulphate was decomposed at room temperature by the addition of copper powder. After this work was completed a different preparation of the tetrahydrophenanthrenecarboxylic acid was reported by Kristensen and Cordier⁴ who recorded the same melting point.

Similarly 2-methylcyclohexenylacetic acid and *o*-nitrobenzaldehyde gave α -2-methylcyclohexenyl-*o*-nitrocinnamic acid, its ethyl ester, and the amino-ester (I; R = Et, R' = Me). The derived diazonium chloride decomposed in water at room temperature on addition of copper powder and hydrolysis of the product gave 5 : 6 : 7 : 8-tetrahydro-8-methylphenanthrene-9-carboxylic acid (II; R = H, R' = Me). The same acid was obtained from the diazonium chloride prepared from *o*-amino- α -2-methylcyclohexenylcinnamic acid (I; R = H, R' = Me). The structure of the tetrahydro-acid was confirmed by dehydrogenation and decarboxylation to 1-methylphenanthrene (III; R' = Me). The formation of tetrahydrophenanthrenes in this manner provides the first examples of a ring closure of

* Part XIII, *J.*, 1959, 1563.

¹ Leake, *Chem. Rev.*, 1956, **56**, 27.

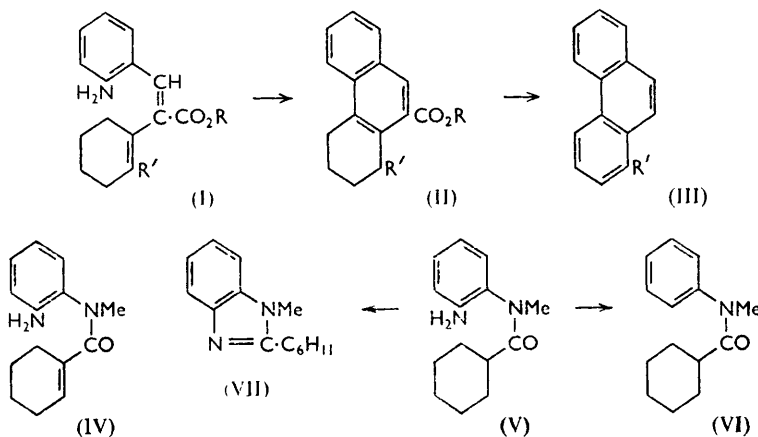
² De Tar, "Organic Reactions," J. Wiley and Sons, Inc., New York, 1957, Vol. IX, p. 409.

³ Schwenk and Papa, *J. Amer. Chem. Soc.*, 1945, **67**, 1432.

⁴ Kristensen and Cordier, *Compt. rend.*, 1956, **242**, 908.

this type with a hydroaromatic system. They also show that the Perkin-type condensations with *cyclohexenylacetic acid* and the aromatic aldehyde give the substituted cinnamic acid in which the carboxyl (ethoxycarbonyl) and nitrophenyl groups are in a *trans*-relation. The actual ring closure probably involves reaction at the α -methylene position in the *cyclohexene* ring and as such is in agreement with the representation of the copper-catalysed reaction as a homolytic process. The work of Waters⁵ and of Farmer and Michael⁶ has shown that the α -methylene position in *cyclohexene* is readily attacked by free radicals.

The inability to obtain *cyclohexylcinnamic acids* by Schwenk and Papa's method³ made it necessary to turn to the phenanthridone series in order to investigate the behaviour in the internuclear cyclisation of a fully reduced ring system. Before proceeding to the hexahydro-series, we prepared *N*-tetrahydrobenzoyl-*N*-methyl-*o*-nitroaniline and reduced it to the amine but catalytic decomposition of the aqueous diazonium chloride prepared from the amino-amide (IV) gave no pure products. On the other hand, reduction of *N*-hexahydrobenzoyl-*N*-methyl-*o*-nitroaniline gave *N*-hexahydrobenzoyl-*N*-methyl-*o*-phenylenediamine (V), which on diazotisation and treatment with copper powder gave *N*-hexahydrobenzoyl-*N*-methylaniline (VI) and an oil which, on the evidence of its infrared spectrum, appeared to contain a carbonyl group. The oil did not appear to contain *N*-methyl-2-oxocyclohexanecarboxyanilide, which was prepared by Sheehan, Goodman, and Hess's



method⁷ using *NN*-dicyclohexylcarbodi-imide for comparison. The application of Sheehan, Goodman, and Hess's method to the preparation of *N*-tetrahydrobenzoyl-*o*-nitroaniline failed, the only products isolated being *NN*-dicyclohexylurea and *N*-tetrahydrobenzoyl-*NN*-dicyclohexylurea (cf. Schulz and Fiedler⁸). When *N*-hexahydrobenzoyl-*N*-methyl-*o*-phenylenediamine (V) was treated in ether with dry hydrogen chloride 2-cyclohexyl-1-methylbenzimidazole (VII) was formed.

EXPERIMENTAL

*Ethyl α -cyclohex-1-enyl-*o*-nitrocinnamate*.—Anhydrous triethylamine (10.1 g.) and acetic anhydride (51 g.) were added to *cyclohex-1-enylacetic acid* (14 g.; prepared in 50% yield by Schwenk and Papa's method;³ m. p. 37°) and *o*-nitrobenzaldehyde (15.1 g.) with stirring, under reflux, and the whole was heated for 12 hr. at 105–110° in dry nitrogen. The mixture was cooled to 60° and the excess of acetic anhydride was decomposed with water. The mixture was

⁵ Waters, *J.*, 1939, 1805.

⁶ Farmer and Michael, *J.*, 1942, 513.

⁷ Sheehan, Goodman, and Hess, *J. Amer. Chem. Soc.*, 1956, **78**, 1368.

⁸ Schulz and Fiedler, *Chem. Ber.*, 1956, **89**, 2681.

then poured on ice, and the semi-solid product was extracted with ether. The extract was washed with water and 5% aqueous sodium carbonate. The alkaline washings were freed from ether, and the hot solution was neutralised with 2N-hydrochloric acid. The neutral solution was heated on a boiling-water bath for 30 min. with charcoal, after which it was filtered and acidified. Recrystallisation of the precipitated acid from aqueous ethanol gave α -cyclohex-1-enyl-o-nitrocinnamic acid (12 g.) in pale yellow needles, m. p. 121° (Found: C, 65.8; H, 5.6. $C_{15}H_{15}O_4N$ requires C, 66.0; H, 5.5%). By the Fischer method the acid (9.9 g.) gave the ethyl ester (7 g.), needles (from aqueous ethanol), m. p. 37.5° (Found: C, 67.8; H, 6.3; N, 4.6. $C_{17}H_{19}O_4N$ requires C, 67.8; H, 6.3; N, 4.7%).

Ethyl o-Amino- α -cyclohex-1-enylcinnamate Hydrochloride.—A mixture of the above ethyl ester (2 g.) and the stannous chloride reagent (20 ml.), prepared as described by Thiele and Dimroth,⁹ was gently warmed for a few minutes and then left at room temperature for 3 hr. The yellow complex which separated was treated with an excess of 2N-aqueous sodium hydroxide until the tin salts had dissolved, leaving the free amine as an oil. The base was extracted with ether, and dry hydrogen chloride was passed into the dried (Na_2SO_4) ethereal solution. The hydrochloride separated and crystallisation from ether-ethanol gave needles (1.5 g.), m. p. 151° (Found: C, 66.0; H, 6.8; N, 4.4. $C_{17}H_{21}O_2N.HCl$ requires C, 66.4; H, 7.2; N, 4.3%).

Decomposition of the Diazonium Fluoroborate prepared from Ethyl o-Amino- α -cyclohex-1-enylcinnamate.—A suspension of the above hydrochloride (3.5 g.) in concentrated hydrochloric acid (20 ml.) and water (60 ml.) was diazotised by sodium nitrite (4 g.) in water (15 ml.). The solution was kept at 0° and filtered. Sodium fluoroborate (5 g.) in water (15 ml.) was added slowly at 0° and the yellow precipitate of the diazonium fluoroborate was collected and dried overnight *in vacuo*. Copper powder (3 g.) was added to a suspension of the dry fluoroborate (2.8 g.) in acetone (200 ml.). There was immediate evolution of nitrogen: the solution was left at room temperature for 3 hr., then warmed and filtered into water, the insoluble residue being extracted several times with acetone and hot water. The combined filtrate and extracts were extracted several times with chloroform. The chloroform solution was washed with 10% aqueous sodium hydroxide and with water and dried (Na_2SO_4). Removal of the chloroform under reduced pressure left a residue (1.8 g.), which was adsorbed from 1:1 benzene-light petroleum (b. p. 60–80°) on an alumina column (100 g.). Elution with 1:1 benzene-light petroleum (b. p. 60–80°) (350 ml.) gave ethyl 5:6:7:8-tetrahydrophenanthrene-9-carboxylate (1.48 g.) as a low-melting solid. Further elution with the same solvent, benzene, ether, and ethanol gave only small quantities of gums. Acidification of the alkaline washings gave a trace of tar. The ethyl ester (1.4 g.) in ethanol (5 ml.) was boiled under reflux for 4 hr. with 10% aqueous potassium hydroxide (50 ml.). The cold solution was washed with ether and acidified with concentrated hydrochloric acid. The acid solution was extracted several times with ether and concentration of the dried (Na_2SO_4) extract deposited 5:6:7:8-tetrahydrophenanthrene-9-carboxylic acid (1.0 g.), which crystallised from aqueous ethanol in plates, m. p. 210° (Found: C, 79.2; H, 6.2. $C_{15}H_{14}O_2$ requires C, 79.6; H, 6.2%), λ_{max} 237, 285, 330–335 m μ (log ϵ 4.73, 3.76, 3.15). A portion of the acid (0.5 g.) was heated with 30% palladium-charcoal (0.2 g.) in a molecular micro-still at 300° for 30 min. Crystallisation of the white sublimate from alcohol gave phenanthrene (0.3 g.) in plates, m. p. and mixed m. p. 100° (picrate, m. p. and mixed m. p. 143–144°).

Decomposition of the Diazonium Sulphate prepared from Ethyl o-Amino- α -cyclohex-1-enylcinnamate.—A suspension of the ester (1.1 g.) in sulphuric acid (5 ml.) and water (30 ml.) was diazotised with sodium nitrite (1 g.) in water (10 ml.) at 0°. After 90 min., the mixture was diluted with water (200 ml.), the yellow diazonium sulphate which had separated redissolving. Urea (2 g.) was added and then copper powder (2 g.), after which the mixture was stirred for 3 hr. at room temperature. The mixture was left overnight and the brown solid which had separated was filtered off. Both filtrate and residue were extracted with ether, and the solvent was removed under reduced pressure from the combined extracts. The residual brown oil was boiled under reflux for 4 hr. with 10% alcoholic potassium hydroxide, after which the solution was diluted with water (400 ml.) and washed with ether. The alkaline solution was neutralised with concentrated hydrochloric acid and heated for 30 min. on a boiling-water bath with charcoal. Filtration and acidification gave 5:6:7:8-tetrahydrophenanthrene-9-carboxylic acid (0.2 g.) in plates, m. p. and mixed m. p. 209–210° (from dilute ethanol).

α -2-Methylcyclohex-1-enyl-o-nitrocinnamic Acid.—Ethyl 2-methylcyclohex-1-enylacetate,

⁹ Thiele and Dimroth, *Annalen*, 1899, 305, 114.

prepared in 56% yield by the general method of Schwenk and Papa,⁹ had b. p. 110—111.5°/14 mm. in agreement with Chuang, Tien, and Ma,¹⁰ and hydrolysis with aqueous-alcoholic potassium hydroxide gave the free acid which solidified in ice (Kon and Thakur¹¹ recorded m. p. 10—14°). 2-Methylcyclohex-1-enylacetic acid (15.4 g.), *o*-nitrobenzaldehyde (15 g.), acetic anhydride (50 g.), and triethylamine (10 g.) were heated on a boiling-water bath in nitrogen for 25 hr., then worked up as described above, giving the acidic products as a brown solid (9 g.). Crystallisation from alcohol gave *o*-nitrocinnamic acid (2.3 g.), m. p. and mixed m. p. 244°. Dilution of the mother-liquor gave α -2-methylcyclohex-1-enyl-*o*-nitrocinnamic acid (5.5 g.), which separated from dilute ethanol in needles, m. p. 144° (Found: C, 66.7; H, 5.4. C₁₆H₁₇O₄N requires C, 67.0; H, 5.9%).

Ethyl o-Amino- α -2-methylcyclohex-1-enylcinnamate.—The above nitro-acid (2 g.) was converted by boiling ethanol containing anhydrous hydrogen chloride into the ethyl ester, b. p. 138°/6 × 10⁻⁴ mm. This (2.0 g.) was reduced with the stannous chloride reagent⁹ (30 ml.) as above. The amino-acid was extracted from ether with concentrated hydrochloric acid. The acid solution was then made alkaline with ice-cooling and extracted with ether. Removal of the ether from the dried extract gave the *amino-ester* (1.0 g.), b. p. 112—117°/6 × 10⁻⁴ mm. (Found: C, 75.9; H, 8.0. C₁₈H₂₃O₂N requires C, 75.8; H, 8.1%).

o-Amino- α -2-methylcyclohex-1-enylcinnamic Acid.—The nitro-acid (1.5 g.) in ethanol (50 ml.) was reduced with hydrogen at atmospheric pressure in the presence of 5% palladium-charcoal (1.0 g.). After the requisite volume of hydrogen had been taken up, the solution was filtered and evaporated to small bulk under reduced pressure. Addition of water deposited *o-amino- α -2-methylcyclohex-1-enylcinnamic acid* (1.2 g.), which crystallised from dilute ethanol in yellow needles, m. p. 173° (Found: C, 75.1; H, 7.0. C₁₆H₁₉O₂N requires C, 74.6; H, 7.4%).

Decomposition of the Diazonium Chloride from Ethyl o-Amino- α -2-methylcyclohex-1-enylcinnamate.—The amino-ester (0.82 g.) in concentrated hydrochloric acid (10 ml.) and water (30 ml.) was diazotised at 0° with sodium nitrite (0.5 g.) in water (20 ml.). The solution was stirred for 3 hr. at 0—5°, after which alcohol (40 ml.) was added and then copper powder (1.0 g.). The mixture was stirred over-night after which reaction with alkaline β -naphthol was negative. The mixture was filtered and both filtrate and residue were extracted with chloroform. The combined chloroform extracts were washed with dilute alkali, dried (Na₂SO₄), and evaporated to a dark oil (0.80 g.), which was chromatographed in 1 : 1 benzene-light petroleum (b. p. 60—80°) on alumina (80 g.). Elution with 1 : 1 benzene-light petroleum (b. p. 40—60°) (200 ml.) gave a white solid, which on hydrolysis with alcoholic potassium hydroxide gave 5 : 6 : 7 : 8-tetrahydro-8-methylphenanthrene-9-carboxylic acid (0.28 g.), plates (from methanol), m. p. 187° (Found: C, 79.9; H, 7.0. C₁₈H₁₈O₂ requires C, 80.0; H, 6.7%), λ_{max} 235, 285, 328—331 μ (log ϵ 4.67, 3.76, 3.07). Further elution with 1 : 1 benzene-light petroleum (b. p. 40—60°) (200 ml.), ether (400 ml.), and alcohol (200 ml.) gave only gums. Acidification of the alkaline extract gave only a trace of tar.

Decomposition of the Diazonium Chloride from o-Amino- α -2-methylcyclohex-1-enylcinnamic Acid.—The amino-acid (1.0 g.) in concentrated hydrochloric acid (10 ml.) and water (20 ml.) was diazotised at 0—5° with sodium nitrite (0.4 g.) in water (20 ml.). The solution was diluted with water (200 ml.) and urea (0.4 g.) was added. The solution was filtered and to the filtrate copper powder (1.0 g.) was added. After being stirred for 2 hr. the mixture no longer gave a positive reaction with alkaline β -naphthol. The solution was filtered and both residue and filtrate were extracted with chloroform. The combined extracts were washed with 10% aqueous sodium hydroxide and the alkaline solution was neutralised and heated on the water-bath for 30 min. with charcoal. It was then filtered and acidified. The precipitated solid (0.4 g.) crystallised from ethanol to give 5 : 6 : 7 : 8-tetrahydro-8-methylphenanthrene-9-carboxylic acid (0.28 g.) in plates, m. p. 187° alone or on admixture with the acid obtained as above. Dehydrogenation and decarboxylation at 300° with palladium-charcoal as described above, and crystallisation of the sublimate from methanol gave 1-methylphenanthrene, m. p. and mixed m. p. 118° (picrate, m. p. and mixed m. p. 136°).

*N-Tetrahydrobenzoyl-*o*-nitroaniline.*—Tetrahydrobenzoic acid (1.7 g.), prepared by Dreiding and Hartman's method,¹² was warmed with an excess of thionyl chloride for 3 hr. after which

¹⁰ Chuang, Tien, and Ma, *Ber.*, 1936, **69**, 1502.

¹¹ Kon and Thakur, *J.*, 1930, 2222.

¹² Dreiding and Hartman, *J. Amer. Chem. Soc.*, 1953, **75**, 942.

the excess was removed under reduced pressure. Pyridine (5 ml.) was added to the well-cooled acid chloride, followed by *o*-nitroaniline (1.9 g.). The mixture was kept at room temperature for 1 hr., then heated on the steam-bath. Dilution with water precipitated *N*-tetrahydrobenzoyl-*o*-nitroaniline (2.3 g.), which crystallised from ethanol in yellow needles, m. p. 68° (Found: C, 63.2; H, 5.4. $C_{13}H_{14}O_3N_2$ requires C, 63.5; H, 5.7%).

N-Tetrahydrobenzoyl-*N*-methyl-*o*-nitroaniline.—The above anilide (4.2 g.) in acetone (40 ml.) and 20% aqueous sodium hydroxide (40 ml.) was boiled under reflux while dimethyl sulphate (8 ml.) was added dropwise. After 15 min. the solution was cooled and diluted with water. The yellow precipitate was collected. Recrystallisation from ethanol gave the *N*-methyl derivative (3.4 g.) in yellow cubes, m. p. 109° (Found: C, 64.7; H, 6.1. $C_{14}H_{16}O_3N_2$ requires C, 64.7; H, 6.1%).

N-Tetrahydrobenzoyl-*N*-methyl-*o*-phenylenediamine.—The above methyl-nitro-compound (0.2 g.) in methanol (100 ml.) was shaken with hydrogen at atmospheric pressure in the presence of 5% palladium-charcoal (0.2 g.) until the required volume of hydrogen had been absorbed. The resulting solution was filtered and evaporated to dryness under reduced pressure. Crystallisation of the residue from methanol gave *N*-tetrahydrobenzoyl-*N*-methyl-*o*-phenylenediamine (0.11 g.) in rhombic needles, m. p. 103° (Found: C, 73.4; H, 7.8. $C_{14}H_{18}ON_2$ requires C, 73.1; H, 7.8%). The aqueous diazonium chloride prepared from this base was treated with copper powder in the usual manner. The product was worked up as in the preceding examples but chromatography gave only gums and tars.

N-Tetrahydrobenzoyl-*NN'*-dicyclohexylurea (cf. ref. 7).—A solution of tetrahydrobenzoic acid (0.8 g.) and *NN'*-dicyclohexylcarbodi-imide (1.3 g.) in methylene dichloride (10 ml.) was kept at room temperature for 2 hr. Dicyclohexylurea, m. p. 216° (0.4 g.), separated. Evaporation of the filtrate gave a gum, which on trituration with water afforded *N*-tetrahydrobenzoyl-*NN'*-dicyclohexylurea (0.4 g.), which crystallised from acetone in needles, m. p. 160–161° (Found: C, 72.4; H, 9.8; N, 8.2. $C_{26}H_{32}O_2N_2$ requires C, 72.3; H, 9.6; N, 8.4%). A similar result was obtained when the reaction was carried out with the addition of *o*-nitroaniline (0.9 g.).

N-Hexahydrobenzoyl-*N*-methyl-*o*-nitroaniline.—(i) Dimethyl sulphate (9 ml.) was added dropwise to a boiling solution of *N*-hexahydrobenzoyl-*o*-nitroaniline¹³ (10 g.) in a mixture of acetone (10 ml.) and 10% aqueous sodium hydroxide (50 ml.). After 10 minutes' boiling the mixture was poured into water. Crystallisation from dilute ethanol of the solid which separated gave *N*-hexahydrobenzoyl-*N*-methyl-*o*-nitroaniline (6.3 g.) in greenish-yellow needles, m. p. 113° (Found: C, 64.2; H, 6.7. $C_{14}H_{18}O_3N_2$ requires C, 64.2; H, 6.9%).

(ii) *cyclo*Hexanecarboxylic acid (4.8 g.) was boiled with thionyl chloride (10 ml.) for 1 hr., after which the excess of thionyl chloride was removed under reduced pressure with the aid of added dry benzene. A cold solution of *N*-methyl-*o*-nitroaniline (5.8 g.) in pyridine (10 ml.) was added to the crude acid chloride cooled in ice. After being left overnight, the mixture was heated on a boiling-water bath for 2 hr., then poured into water (100 ml.). Recrystallisation from dilute ethanol of the precipitated solid gave *N*-hexahydrobenzoyl-*N*-methyl-*o*-nitroaniline (4.3 g.) in greenish-yellow needles m. p. 113°, identical with the specimen prepared by method (i).

N-Hexahydrobenzoyl-*N*-methyl-*o*-phenylenediamine.—The above nitro-compound (1.6 g.) in methanol (100 ml.) containing 5% palladium-charcoal (0.2 g.) was shaken with hydrogen at atmospheric pressure until the required volume had been absorbed. After filtration the solvent was removed under reduced pressure. Trituration of the residual brown oil with light petroleum (b. p. 40–60°) gave *N*-hexahydrobenzoyl-*N*-methyl-*o*-phenylenediamine (0.85 g.), which crystallised from benzene-light petroleum (b. p. 40–60°) in needles, m. p. 93.5° (Found: C, 72.7; H, 8.5. $C_{14}H_{20}ON_2$ requires C, 72.6; H, 8.6%). When a stream of dry hydrogen chloride was passed into a solution of this base (2.0 g.) in dry ether (20 ml.) 2-cyclohexyl-1-methylbenzimidazole (1.1 g.) separated in needles, m. p. 104° (Found: C, 78.6; H, 8.5. $C_{14}H_{18}N_2$ requires C, 78.4; H, 8.4%).

Decomposition of the Diazonium Chloride from N-Hexahydrobenzoyl-*N*-methyl-*o*-phenylenediamine.—The amine (7.7 g.), suspended in concentrated hydrochloric acid (20 ml.) and water (150 ml.), was diazotised at 0–5° with sodium nitrite (3.3 g.) in water (40 ml.). During the diazotisation ethanol (50 ml.) was added and stirring was continued for 3 hr., after which urea (3.5 g.) was added, followed by copper powder (2 g.). There was an immediate evolution of nitrogen. The mixture was stirred at room temperature overnight (negative reaction with alkaline β -naphthol), then worked up as in the previous case. The resulting red oil was chromatographed in 1 : 2 benzene-light petroleum (b. p. 40–60°) on alumina (90 g.). Elution with

¹³ Herbst, Roberts, Givens, and Harvill, *J. Org. Chem.*, 1952, **17**, 262.

the same solvent (200 ml.) yielded a colourless gum (*A*) (1.8 g.) after which elution with a 1 : 1 mixture (300 ml.) gave *N*-hexahydrobenzoyl-*N*-methylaniline (0.8 g.), needles (from dilute methanol), m. p. 62.5° (Found: C, 77.1; H, 8.3. C₁₄H₁₈ON requires C, 77.6; H, 8.3%), identical with a specimen prepared from cyclohexanecarboxyl chloride and *N*-methylaniline in pyridine. Further elution with ether (350 and 200 ml.) and with alcohol (200 ml.) gave gums (0.2 g., 0.3 g., and 1.1 g. respectively). The infrared spectrum of fraction (*A*) indicated the presence of carbonyl (1715 cm.⁻¹) and amide (1668 cm.⁻¹) groups. This fraction was distilled at 87°/0.1 mm. and the distillate (1.3 g.) was again chromatographed in 1 : 2 benzene–light petroleum (b. p. 40–60°) on alumina. Elution with the same solvent (150, 50, and 50 ml.) gave gums (*a–c*) (0.1, 0.02, and 0.03 g. respectively). Further elution with the same solvent (100 ml.) gave a gum from which *N*-hexahydrobenzoyl-*N*-methylaniline (0.5 g.), m. p. 62.5°, separated. The infrared spectra of the first three fractions showed a strong band at 1715 cm.⁻¹ but the band at 1668 cm.⁻¹ was considerably diminished. Further chromatography of the fractions (*a*) and (*b*) gave a ketonic product, which showed strong absorption at 1715 and a weak band at 1650 cm.⁻¹ (Found: C, 76.3; H, 8.1; N, 5.85%). *N*-Hexahydrobenzoyl-*N*-methylaniline shows no absorption at 1715 cm.⁻¹ but strong bands at 1667 and 704 cm.⁻¹.

N-Methyl-2-oxocyclohexanecarboxyanilide.—2-Oxocyclohexanecarboxylic acid (1.1 g.), methylaniline (0.83 g.), and *NN'*-dicyclohexylcarbodi-imide ⁷ (1.6 g.) were dissolved in methylene dichloride. *NN'*-Dicyclohexylurea was immediately precipitated. After 2 hr. the solution was filtered and the filtrate was washed successively with *n*-hydrochloric acid, aqueous potassium hydrogen carbonate, and water. Removal of the solvent from the dried (Na₂SO₄) solution left an oil, which was adsorbed from benzene on alumina. Elution with benzene gave *N*-methyl-2-oxocyclohexanecarboxyanilide (0.8 g.), b. p. 115–120°/0.10–0.13 mm. (Found: C, 72.9; H, 8.0. C₁₄H₁₇O₂N requires C, 72.8; H, 7.4%), having strong infrared absorption at 1715, 1668, 779, and 704 cm.⁻¹.

The authors thank Dr. J. W. Cook, F.R.S., for a specimen of 1-methylphenanthrene, also British Celanese, Ltd., for the award of a Studentship (to R. A. J. L.).

KING'S COLLEGE (UNIVERSITY OF LONDON),
STRAND, LONDON, W.C.2.

[Received, January 21st, 1959.]