# 2-*Acyl*cyclo*hexane*-1 : 3-*diones. Part II.** 2-*Formyl-*, 2-*Propionyl-*, 2-iso-*Butyryl-*, *and* 2-*Phenylcarbamoyl-*cyclo*hexane*-1 : 3-*dione, and their Conversion into Phenanthridines.*

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Some 2-acyl*cyclo*hexane-1 : 3-diones have been prepared by the action of acid anhydrides and boron trifluoride on *cyclo*hexane-1 : 3-dione; 2-formyl-*cyclo*hexane-1 : 3-dione was obtained by hydrolysis of *N*-2 : 6-dioxo*cyclo*-hexylmethyleneaniline, produced by fusing *cyclo*hexane-1 : 3-dione with *NN'*-diphenylformamidine. 2-Propionyl*cyclo*hexane-1 : 3-dione with aniline gave *N*-2 : 6-dioxo*cyclo*hexylpropylideneaniline which afforded 9-ethyl-5 : 6 : 7 : 8-tetrahydro-8-oxophenanthridine, but 2-*iso*butyryl*cyclo*hexane-1 : 3-dione failed to react. Neither 2 : 6-dioxo*cyclo*hexylmethyleneaniline nor 2-phenylcarbamoyl*cyclo*hexane-1 : 3-dione (prepared from the sodium derivative of *cyclo*hexane-1 : 3-dione and phenyl *iso*cyanate) gave a cyclodehydration product.

IN Part I * were described the preparation of 2-acetyl*cyclo*hexane-1 : 3-dione (I; R = Me) and its reaction with aniline to give exclusively 1-(2 : 6-dioxo*cyclo*hexyl)ethylideneaniline (II; R = Me) which afforded a tetrahydromethyloxophenanthridine. This synthesis is a useful modification of Borsche's (*Annalen*, 1910, **377**, 70) and the present work is an attempt to extend it.

2-Propionyl*cyclo*hexane-1 : 3-dione was first prepared by the method of Part I, from *cyclo*hexane-1 : 3-dione, propionic anhydride, and sodium propionate. The yield was low (13%) and, although improved (to 19%) by use of pyridine as catalyst, indicated that for larger acyl groups other methods of preparation might be preferable. Only 3-acyloxy-*cyclo*hex-2-enones resulted from reaction of acetyl chloride with the sodium derivative of *cyclo*hexane-1 : 3-dione and of the ethoxymagnesium derivative of *cyclo*hexane-1 : 3-dione with acyl chlorides, although the latter method caused *C*-acylations of acetoacetic ester (Viscontini and Merckling, *Helv. Chim. Acta*, 1952, **35**, 2288; Dean, Halewood, Mongkolsuk, Robertson, and Whalley, *J.*, 1953, 1250).

Acylation of *cyclo*hexane-1 : 3-diones with acid anhydrides in the presence of boron trifluoride (Meerwein and Vossen, *J. prakt. Chem.*, 1934, **141**, 149; Dean and Robertson, *J.*, 1953, 1241) had moderate success. Since the dione is insoluble in cold liquid anhydrides the corresponding acids were used as solvents. With this modification the ketones (I; R = Me, Et, and $\mathrm{Pr^i}$) were obtained in yields of 23, 71, and 24% respectively. From these results and those of Meerwein and Vossen (*loc. cit.*) it appears that the yield of triketone is controlled by opposing factors, namely, the size of the entering acyl group and the tendency of the anhydride to condense with itself. Octanoic anhydride (also a liquid at room temperatures) gave only a 2% yield. Benzoic anhydride in chloroform gave a white solid, probably its boron trifluoride complex (cf. Greenwood and Martin, *Quart. Reviews*, 1954, **8**, 1), but no triketone was isolated. Phenylacetic anhydride gave a low yield (8%).

2-Formyl*cyclo*hexane-1 : 3-dione (I; R = H), the first member of the series, was not formed by Claisen condensation of *cyclo*hexane-1 : 3-dione and ethyl formate, probably because *cyclo*hexane-1 : 3-dione is a very strong acid ($K_a \sim 5{\cdot}5 \times 10^{-6}$) (probably stronger than the desired product) and has an unreactive anion. 3-Formyloxy*cyclo*hex-2-enone, which under basic conditions might be rearranged to the *C*-acyl derivative (cf. Wislicenus and Koerler, *Ber.*, 1901, **34**, 218, 3768; Dieckmann and Stein, *Ber.*, 1904, **37**, 3370), could not be prepared by direct or ester-exchange methods. Dains *et al.* (*Ber.*, 1902, **35**, 2496 *et seq.*) showed that *NN'*-diphenylformamidine condenses with compounds containing

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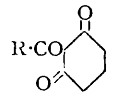
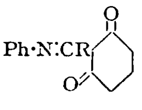
* "2-Acetyl*cyclo*hexane-1 : 3-dione," Smith, *J.*, 1953, 803, is regarded as Part I of this series.

reactive methylene groups to give what were described as anilinomethylene derivatives although by prototropy they might equally be methyleneanils. The methyleneanil from *cyclo*hexane-1 : 3-dione was hydrolysed by 2% aqueous sodium carbonate (Mansberg and Shaw, *J.*, 1953, 3467) to the desired triketone (I; R = H), an unstable oil, which however could be recrystallised at −70°.


(I)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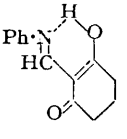
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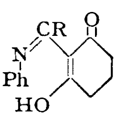
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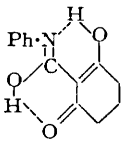
(V)

2-Propionyl*cyclo*hexane-1 : 3-dione and aniline in boiling ethanol gave a good yield of a single anil, which is 1-(2 : 6-dioxo*cyclo*hexyl)propylideneaniline of structure (II; R = Et) since it gives no colour with ferric chloride and is converted by the method of Part I (*loc. cit.*) into 9-ethylphenanthridine (Pictet and Hubert, *Ber.*, 1896, **29**, 1186). 2-*iso*-Butyryl*cyclo*hexane-1 : 3-dione (I; R = $Pr^i$) could not be induced to react with aniline. The failure of the ring carbonyl groups to react with aniline may be contrasted with the reactivity of both carbonyl groups in 2-acetyl*cyclo*hexan-1-one (Borsche, *loc. cit.*). When in 2-acyl*cyclo*hexane-1 : 3-diones the carbonyl group in the side-chain is sterically hindered, as in (I; R = $Pr^i$), no reaction with normal carbonyl reagents occurs : protokosin which contains a similar grouping also failed to give carbonyl derivatives (Hems and Todd, *J.*, 1937, 562).

2-Formyl*cyclo*hexane-1 : 3-dione reacted readily with aniline, even in the cold, to give the anil (II; R = H) formed from *NN'*-diphenylformamidine and *cyclo*hexane-1 : 3-dione. This anil, like its analogues (II; R = Me and Et), was soluble in alkali and gave no colour with ferric chloride, but unlike them it gave a copper complex and did not undergo cyclodehydration to a tetrahydro-oxophenanthridine with phosphoric anhydride–phosphoric acid or anhydrous hydrofluoric acid. Failure of the cyclodehydration is typical of anils of β-keto-aldehydes (Claisen and Fischer, *Ber.*, 1888, **21**, 1135; Thielpape, *Ber.*, 1922, **55**, 127; Romet, *Compt. rend.*, 1935, **200**, 1676; Borsche, *loc. cit.*) where it is attributed to the supposed *trans*-configuration about the C=N linkage as compared with the *cis*-configuration thought to be present in the cyclisable anils of β-diketones (Thielpape, *loc. cit.*).

The same explanation may apply to the anil (II; R = H) where complex formation would be favoured by a structure such as (III) and sterically hindered by (IV; R = H) although as Calf and Ritchie (*J. Proc. Roy. Soc. New South Wales*, 1949, **83**, 117) have pointed out, a difference in configuration is not necessarily sufficient to explain the failure of the anils of β-keto-aldehydes to undergo cyclodehydration. Study of the infra-red absorption spectrum of (II; R = H) supports the *trans*-structure since it indicates a chelated carbonyl group (bands at 6·0 and 6·35 μ). The spectra of the anil (II; R = Me) [bands at 6·15 and 6·38 μ (Part I, *loc. cit.*)] and (II; R = Et) (bands at 6·10 and 6·35 μ) are, however, similar in the carbonyl region to those for 2-methyl- and 2-ethyl-*cyclo*hexane-1 : 3-dione [both with bands at 6·10 and 6·35 μ (Part I, *loc. cit.*)] in which chelation is impossible.

Petrow and Hollingsworth (*J.*, 1948, 1537) found that 2'-oxo*cyclo*hexylmethylene-1-naphthylamine was converted into 3 : 4 : 5 : 6-tetrahydro-1-azachrysene by prolonged heating in anhydrous formic acid, supposedly by primary reduction of the C=N bond. By this method the anil (II; R = H), however, gave only a tar, nor was the reduced product formed by magnesium in ethanol (Zechmeister and Truka, *Ber.*, 1930, **63**, 2883) or by hydrogen in the presence of Raney nickel in ethanol. In the last reaction hydrogenolysis to 2-methyl*cyclo*hexane-1 : 3-dione occurred and the analogue (II; R = Me) was similarly converted into 2-ethyl*cyclo*hexane-1 : 3-dione, probably because saturation of the double bond would give a Mannich base and it is known that Mannich bases of phenols are readily hydrogenolysed to alkylphenols (Caldwell and Thompson, *J. Amer. Chem. Soc.*, 1939, **61**, 765).

A further attempt to prepare a tetrahydro-1-oxophenanthridine unsubstituted in the 9-position led to an additional triketone. Phenyl *iso*cyanate condenses with compounds containing an active methylene group or their sodium salts to give *C*- rather than *O*-substituted products (Michael, *J. prakt. Chem.*, 1887, **35**, 451; Behrend and Mayer, *Ber.*, 1900, **33**, 623; Dieckmann, *ibid.*, p. 2002; Michael and Cobb, *Annalen*, 1908, **363**, 64; Steinkopf and Daege, *Ber.*, 1911, **44**, 497). The sodium derivative of *cyclo*hexane-1 : 3-dione with phenyl *iso*cyanate in tetrahydrofuran gave 2-phenylcarbamoyl*cyclo*hexane-1 : 3-dione (I; R = NHPh), whose structure follows from its ability to form a copper complex. The triketone decomposed in concentrated sulphuric acid or phosphoric acid–phosphoric anhydride and was recovered unchanged after treatment with anhydrous hydrofluoric acid, although 2-phenylcarbamoyl- (Blount, Perkin, and Plant, *J.*, 1929, 1975) and 2-1′-naphthylcarbamoyl-*cyclo*pentan-1-one (Clemo and Mishra, *J.*, 1953, 192) both cyclise readily to α-quinolones. The ultra-violet absorption spectrum of the carbamoyl compound (I; R = NHPh), unlike that of the 2-acyl*cyclo*hexane-1 : 3-diones, shows no band in the 230—240 mμ region, only an intense band at 270 mμ. This indicates that, in solution at least, it exists as the imidoyl form (V) or a bond isomer which would be stabilised by double chelation, and, containing no αβ-unsaturated ketone grouping, would show no absorption in the 230—240 mμ region (cf. Part I, *loc. cit.*). The intense band at 270 mμ is in accord with the extended system of conjugation present in (V) or its bond isomer.

The anil from the triketone (I; R = Me) and 1-aminonaphthalene was best obtained by Redelien's method (*Annalen*, 1912, **388**, 165). It was cyclised to 3 : 4 : 5 : 6-tetrahydro-2-methyl-3-oxo-1-azachrysene which on reduction and dehydrogenation gave 2-methyl-1-azachrysene (Ritchie, *J. Proc. Soc., N.S.W.*, **1945**, **78**, 186). The methyl group in the latter can be replaced by hydrogen (Ritchie, *ibid.*, 1944, **78**, 164; Caldwell, *J.*, 1952, 2035) and so the above synthesis offers a practical route to the 1-azachrysene system which is present in various plant alkaloids.

## EXPERIMENTAL

Infra-red spectra were determined for solids as Nujol mulls and for liquids as liquid films. All spectra were determined by Dr. F. B. Strauss with the technical assistance of Mr. F. Hastings.

2-*Propionyl*cyclo*hexane*-1 : 3-*dione* (I; R = Et).—(i) *cyclo*Hexane-1 : 3-dione (35 g.) and anhydrous sodium propionate (6·5 g.) were heated in propionic anhydride (235 g.) at 125° (bath) for 7·5 hr. The anhydride was removed under reduced pressure, the tarry residue was extracted with alkali, and the extracts were acidified. The resulting gum was collected with ether and distilled in steam until the distillate gave no colour with ferric chloride. The distillate was thoroughly extracted with ether, and the extract was washed with water and shaken with an excess of aqueous copper acetate. The copper complex (8·1 g., 13%), m. p. 185° (from chloroform), was filtered off and shaken with 3N-hydrochloric acid (150 c.c.) and ether (200 c.c.). The ethereal solution was washed with water, dried ($MgSO_4$), and evaporated under reduced pressure. Distillation then gave colourless 2-*propionyl*cyclo*hexane*-1 : 3-*dione* (6·3 g.), b. p. 124°/15 mm., m. p. 19° (Found: C, 64·1; H, 7·3. $C_9H_{12}O_3$ requires C, 64·4; H, 7·2%). Light absorption in MeOH: Max. 235 and 275 mμ (ε 9300 and 8300). The infra-red spectrum had bands at 6·00 and 6·40 μ.

(ii) A solution of *cyclo*hexane-1 : 3-dione (5 g.) in propionic acid (20 g.) and propionic anhydride (20 g.) was added dropwise during 1·5 hr. to propionic anhydride (20 g.) and pyridine (2 g.) at the b. p. Refluxing was continued for a further 4·5 hr., then the solvents were removed under reduced pressure. The residue was dissolved in ether, filtered off, washed with water, and shaken with saturated cupric acetate solution. The precipitate was filtered off, dried, and recrystallised from chloroform, to give 2-propionyl*cyclo*hexane-1 : 3-dione copper complex (1·7 g., 19%), m. p. 185°, undepressed by a sample prepared as in (i). Similarly *cyclo*hexane-1 : 3-dione and acetic anhydride gave a 34% yield of 2-acetyl*cyclo*hexane-1 : 3-dione copper complex, m. p. 265°, undepressed on admixture with a sample prepared as described in Part I (*loc. cit.*).

(iii) A solution of *cyclo*hexane-1 : 3-dione (5·2 g.) in propionic anhydride (12·5 g.) and propionic acid (15 g.) was saturated with boron trifluoride (ice-cooling), 17·5 g. being absorbed. Sodium acetate (35 g.) in water (50 c.c.) was added and the mixture distilled in steam until it gave no ferric chloride colour. Working up as under (i) gave 2-propionyl*cyclo*hexane-1 : 3-dione copper complex (6·6 g., 71%), m. p. 185°, undepressed by the sample prepared as in (i). The same method gave a 23% yield of 2-acetyl*cyclo*hexane-1 : 3-dione copper complex, m. p. 265°.

2-iso*Butyryl*cyclo*hexane*-1 : 3-*dione* (I; R = $Pr^i$).—A solution of *cyclo*hexane-1 : 3-dione (20 g.) in *iso*butyric anhydride (43 g.) and *iso*butyric acid (40 g.) was saturated with boron trifluoride, and the treated was treated as above. The steam distillate was extracted with ether, and the ethereal solution washed with sodium hydrogen carbonate solution to remove acid, then with water, and was shaken with saturated aqueous cupric acetate. The 2-iso*butyryl*cyclo*hexane*-1 : 3-*dione copper complex* (9·25 g., 24%) had m. p. 228—230° after recrystallisation from aqueous ethanol (Found : C, 56·2; H, 6·4. $C_{20}H_{26}O_6Cu$ requires C, 56·3; H, 6·4%). The complex was decomposed in the usual manner and the product distilled, to give the 2-iso*butyryl*cyclo*hexane*-1 : 3-*dione* (7·25 g.), b. p. 144°/20 mm., m. p. 37—38° (Found : C, 65·9; H, 7·8. $C_{10}H_{14}O_3$ requires C, 65·9; H, 7·7%). Light absorption in MeOH : Max. 235 and 275 mμ (ε 14,000 and 13,350). The infra-red spectrum had bands at 6·00 and 6·40 μ.

2-*Octanoyl*cyclo*hexane*-1 : 3-*dione* (I; R = $C_7H_{15}$).—A solution of *cyclo*hexane-1 : 3-dione (10 g.) in octanoic anhydride (20 g.; cf. Gerrard and Thrush, *J.*, 1952, 741) and octanoic acid (20 g.) was saturated with boron trifluoride. The mixture was treated with sodium acetate (70 g.) in water (100 c.c.), and then distilled in steam to remove most of the acid. The residue was extracted with ether, and the ether washed with sodium hydrogen carbonate solution and water and shaken with saturated aqueous cupric acetate. The green precipitate was filtered off, washed with ether to remove any copper hexanoate, and decomposed in the known manner to an oil, which was dissolved in a little light petroleum (b. p. 40—60°). Chilling at −70° precipitated a buff solid, m. p. 46°, which we did not identify. The residual oil was distilled, to give the 2-*octanoyl*cyclo*hexane*-1 : 3-*dione* (0·26 g.), b. p. 100° (bath-temp.)/0·1 mm. (Found : C, 70·2; H, 9·2. $C_{14}H_{22}O_3$ requires C, 70·6; H, 9·2%). Light absorption in MeOH : Max. 232·5 and 275 mμ (ε = 10,400 and 9900). The infra-red spectrum had bands at 6·00 and 6·45 μ. The *copper complex* prepared from the pure trione had m. p. 132—136° (sealed capillary) after recrystallisation from chloroform–light petroleum (b. p. 60—80°) (Found: C, 62·4; H, 7·7. $C_{28}H_{42}O_6Cu$ requires C, 62·4; H, 7·8%).

2-*Phenylacetyl*cyclo*hexane*-1 : 3-*dione* (I; R = $CH_2Ph$).—A solution of *cyclo*hexane-1 : 3-dione (1·6 g.) and phenylacetic anhydride (3·5 g., Wedekind, *Ber.*, 1901, **34**, 2070) in chloroform (15 c.c.) was saturated with boron trifluoride. The dark solution was treated with 70% aqueous sodium acetate and extracted with ether. The ethereal solution was washed with sodium hydrogen carbonate solution and water, concentrated, and shaken with saturated aqueous cupric acetate. The copper complex (0·3 g., 8%) had m. p. 182—185° after recrytallisation from chloroform. It was decomposed in the usual manner to yield a solid which separated from light petroleum (b. p. 40—60°) as colourless needles, m. p. 79°, b. p. 175° (bath-temp.)/ 15 mm. (Found : C, 72·7; H, 6·1. $C_{14}H_{14}O_3$ requires C, 73·1; H, 6·1%). Light absorption in MeOH : Max. 235 and 275 mμ (ε 15,200 and 15,200). The infra-red spectrum had bands at 6·03 and 6·43 μ.

2 : 6-*Dioxo*cyclo*hexylmethyleneaniline* (II; R = H).—A mixture of *cyclo*hexane-1 : 3-dione (15·5 g.) and *NN'*-diphenylformamidine (31 g.) was heated at 130° (bath-temp.) for 1 hr. After cooling, the product was extracted with 5% hydrochloric acid (200 c.c.), washed with water, dried, and recrystallised from light petroleum (b. p. 60—80°) to give 2 : 6-*dioxo*cyclo*hexylmethyleneaniline* as yellow needles (25 g.), m. p. 124—125° (Found : C, 72·2; H, 6·0; N, 6·4. $C_{13}H_{13}O_2N$ requires C, 72·6; H, 6·1; N, 6·5%). The infra-red spectrum had bands at 6·00 and 6·35 μ. The anil was soluble in alkali, reprecipitated on acidification, and soluble in excess of acid. In ether it gave with aqueous cupric acetate a green *copper complex*, m. p. 260—262°, after recrystallisation from chloroform–light petroleum (b. p. 60—80°) (Found : N, 5·2. $C_{26}H_{24}O_4N_2Cu$ requires N, 5·7%). *NN'*-Diphenylacetamidine failed to condense with *cyclo*hexane-1 : 3-dione under the above conditions.

2-*Formyl*cyclo*hexane*-1 : 3-*dione* (I; R = H).—A suspension of the above anil (18 g.) in 2% sodium carbonate solution was boiled in an open vessel, the volume being kept constant by occasional addition of water, until the steam gave no colour with sodium hypochlorite paper. The mixture was then cooled, acidified, saturated with salt, and extracted with ether. The ethereal solution was washed with brine and shaken with saturated aqueous cupric acetate, affording a copper complex which was decomposed in the usual way. The resulting oil was extracted with boiling light petroleum (b. p. 40—60°) until only a resin remained, and the extracts were combined and chilled at −70°. The supernatant liquid was decanted from the mass of colourless crystals, which liquefied on regaining room temperature. The resulting 2-*formyl*cyclo*hexane*-1 : 3-*dione* (8·2 g.) was freed from solvent *in vacuo* (Found : C, 59·7; H, 6·0. $C_7H_8O_3$ requires C, 60·0; H, 5·7%). The triketone resinified when an attempt was made to distil it in bulk, but a small quantity could be distilled with only slight darkening [b. p. 105° (bath-temp.)/12 mm.]. Light absorption in MeOH : Max. 240 and 255 mμ (ε = 9100 and 9800). The infra-red spectrum had a strong band at 5·98, and a very broad, intense band centred at 6·30 μ. When the trione (1·5 g.) was treated with aniline (1·1 g.) in ethanol (5 c.c.), yellow needles began to separate almost immediately. The reaction was completed by a few minutes' warming on the steam-bath, the mixture was cooled, and the crystals were filtered off. Recrystallisation from light petroleum (b. p. 60—80°) gave the 2 : 6-dioxo*cyclo*hexylmethyleneaniline as needles (1·6 g.), m. p. 124°, undepressed by a sample prepared as described above and possessing an identical infra-red absorption spectrum. Light absorption in MeOH : Max. 235, 255, and 340 mμ (ε 9000, 9600, and 23,700). This spectrum is different from that for the anils [II; R = Me (Part I, *loc. cit.*) and Et (below)] and is in accord with the *trans*-formulation (III) for the anil. 2-Formyl*cyclo*hexane-1 : 3-dione did not react with *N*-methylaniline in ethanol.

1-(2 : 6-*Dioxo*cyclo*hexyl*)*propylideneaniline* (II; R = Et).—2-Propionyl*cyclo*hexane-1 : 3-dione (2·5 g.) was refluxed in ethanol (12 c.c.) with aniline (2·0 g.) for 5 hr. The solution was poured into water (100 c.c.). The precipitate, after solidification, was dried and recrystallised from light petroleum (b. p. 60—80°) to give the 1-(2 : 6-*dioxo*cyclo*hexyl*)*propylideneaniline* as colourless needles (2·7 g.), m. p. 74° (Found : C, 74·1; H, 7·1; N, 6·0. $C_{15}H_{17}O_2N$ requires C, 74·1; H, 7·0; N, 5·8%). Light absorption in MeOH : Max. 250 and 305 mμ (ε = 17,000 and 19,900). The infra-red spectrum had bands at 6·10 and 6·35 μ.

9-*Ethyl*-5 : 6 : 7 : 8-*tetrahydro*-8-*oxophenanthridine*.—1-(2 : 6-Dioxo*cyclo*hexyl)propylideneaniline (2·5 g.) was heated at 180° with phosphoric anhydride (19 g.) and phosphoric acid (28 g.) for 1 hr. On cooling to 90°, the mixture was poured into water, basified, and extracted with ether, and the ethereal solution washed with water, dried ($MgSO_4$), and evaporated under reduced pressure. The crystalline residue was recrystallised from light petroleum to give the 9-*ethyl*-5 : 6 : 7 : 8-*tetrahydro*-8-*oxophenanthridine* as buff needles (1·5 g.), m. p. 77° (Found : C, 80·0; H, 6·6; N, 6·2. $C_{15}H_{15}ON$ requires C, 80·0; H, 6·7; N, 6·2%). Light absorption in MeOH : Max. 240, 285, and 325 mμ (ε = 28,600, 8300, and 1300). The infra-red spectrum had a band at 5·95 μ.

9-*Ethyl*-5 : 6 : 7 : 8-*tetrahydro*-8-*hydroxyphenanthridine*.—The above ethyltetrahydro-oxophenanthridine (0·8 g.) in dry ether (60 c.c.) was refluxed with lithium aluminium hydride (0·3 g.) in ether (80 c.c.) for 30 min. 9-*Ethyl*-5 : 6 : 7 : 8-*tetrahydro*-8-*hydroxyphenanthridine* was obtained from ethyl acetate–light petroleum (b. p. 60—80°) as needles (0·20 g.), m. p. 114° (Found : N, 5·8. $C_{15}H_{17}ON$ requires N, 6·1%). Light absorption in MeOH : Max. 235, 275, 305, and 320 mμ (ε 25,600, 5300, 4200, and 3200). The infra-red spectrum had bands at 2·80, 3·05, and 3·25 μ.

9-*Ethylphenanthridine*.—The preceding compound (130 mg.) was heated with 30% palladised charcoal (20 mg.) at 260° for 25 min. The dark residue was extracted with warm ether (4 × 20 c.c.) and boiling ethanol (20 c.c.), and the extracts were combined, dried, and evaporated to a gum which was extracted with boiling light petroleum (b. p. 60—80°; 4 × 20 c.c.). The product was passed in light petroleum (b. p. 40—60°) through activated alumina (5 g.). The resulting oil crystallised and gave 9-ethylphenanthridine as colourless needles (40 mg.), m. p. 55·5°, from light petroleum (b. p. 40—60°) (Found : C, 86·6; H, 6·4; N, 6·7. Calc. for $C_{15}H_{13}N$ : C, 87·0; H, 6·3; N, 6·8%). Light absorption in MeOH : Max. 250, 300, 345, and 365 mμ (ε 33,100, 5700, 4100, and 4100). Pictet and Hubert (*loc. cit.*) give 54—55°.

2-*Methyl*cyclo*hexane*-1 : 3-*dione*.—2 : 6-Dioxo*cyclo*hexylmethyleneaniline (1 g.) in ethanol (30 c.c.) containing freshly prepared Raney nickel was shaken with hydrogen until 1 mol. had been absorbed. The catalyst was filtered off, the filtrate evaporated under reduced pressure, and the residue washed with a little dry benzene. The product, recrystallised from benzene, gave 2-methyl*cyclo*hexane-1 : 3-dione (0·20 g.), m. p. and mixed m. p. 206°, possessing the authentic infra-red absorption spectrum. The benzene washings were evaporated to a gum which was extracted with boiling light petroleum (b. p. 60—80°). The extracts deposited unchanged 2 : 6-dioxo*cyclo*hexylmethyleneaniline, m. p. 122°.

2-*Ethyl*cyclo*hexane*-1 : 3-*dione*.—1-(2 : 6-Dioxo*cyclo*hexyl)ethylideneaniline (0·5 g.) was hydrogenated at 1 atm. in ethanol (25 c.c.) over Raney nickel until 2 mols. had been absorbed (12 hr.). 2-Ethyl*cyclo*hexane-1 : 3-dione was obtained from benzene as leaflets (0·15 g.), m. p. 176° (Found : C, 68·7; H, 8·5. Calc. for $C_8H_{12}O_2$ : C, 68·6; H, 8·6%).

2-*Phenylcarbamoyl*cyclo*hexane*-1 : 3-*dione* (I; R = NHPh).—*cyclo*Hexane-1 : 3-dione (3 g.) in methanol (20 c.c.) was added to sodium methoxide (from the metal, 0·55 g.) in methanol, and the solution evaporated to dryness under reduced pressure. The resulting sodium salt was finely powdered by shaking, and refluxed in suspension, in pure tetrahydrofuran (40 c.c.)

with phenyl *iso*cyanate (3 g.) for 3 hr. The solvent was removed under reduced pressure and the residue decomposed with dilute acid. The mixture was extracted with ether, and the ethereal solution washed with water and shaken with saturated aqueous cupric acetate. The 2-*phenylcarbamoyl*cyclo*hexane*-1 : 3-*dione copper complex* (5·1 g.), m. p. 277° (decomp.), was insoluble in chloroform (Found : N, 5·3. $C_{26}H_{24}O_6N_2Cu$ requires N, 5·3%). It was decomposed in the usual way to give 2-*phenylcarbamoyl*cyclo*hexane*-1 : 3-*dione* separating from ethanol as buff prisms (4·1 g.), m. p. 77° (Found : C, 67·5; H, 6·0; N, 6·0. $C_{13}H_{13}O_3N$ requires C, 67·5; H, 5·7; N, 6·0%). Light absorption (methanol) : Max. 270 mμ (ε 20,600). The infra-red spectrum had bands at 6·06, 6·30, and 6·48 μ. The product was soluble in alkali and gave a blood-red colour with ferric chloride.

1′-(2 : 6-*Dioxo*cyclo*hexyl*)*ethylidene*-1-*naphthylamine*.—(i) 2-Acetyl*cyclo*hexane-1 : 3-dione (1·53 g.) and 1-naphthylamine (1·55 g.) were refluxed in ethanol (10 c.c.) for 6 hr. When cold, the solution was poured into water and the precipitate was filtered off, dried, and recystallised from ethyl acetate–light petroleum (b. p. 60—80°) to give the *anil* as needles (1·35 g.), m. p. 144—145° (Found : C, 77·1; H, 6·2; N, 5·3. $C_{18}H_{17}O_2N$ requires C, 77·4; H, 6·1; N, 5·0%). Light absorption in MeOH : Max. 225, 250, and 310 mμ (ε 28,700, 16,600, and 18,900). The anil was soluble in alkali and gave no colour with aqueous-ethanolic ferric chloride.

(ii) 1-Naphthylamine–zinc chloride complex (0·1 g.), prepared by grinding powdered zinc chloride (1 mol.) with 1-naphthylamine (2 mols.) on the steam-bath, was added to acetyl*cyclo*hexane-1 : 3-dione (1·25 g.) and 1-naphthylamine (1·1 g.) at 150°, vigorous evolution of steam occurring. The temperature was raised to 180° during 30 min. and the mixture, on cooling, was extracted with chloroform. The combined extracts were filtered. The product was recrystallised from ethanol to give the above anil (1·6 g.), m. p. 144—145°.

3 : 4 : 5 : 6-*Tetrahydro*-2-*methyl*-3-*oxo*-1-*azachrysene*.—The above anil (1·2 g.) was cyclised in the usual way with phosphoric anhydride (9·5 g.) and phosphoric acid (8 c.c.) at 170°. 3 : 4 : 5 : 6-*Tetrahydro*-2-*methyl*-3-*oxo*-1-*azachrysene*, from ethyl acetate–light petroleum (b. p. 60—80°), formed buff needles (0·75 g.), m. p. 154° (Found : C, 82·8; H, 5·8; N, 5·4. $C_{18}H_{15}ON$ requires C, 82·5; H, 5·8; N, 5·4%). Light absorption in MeOH : Max. 235, 270, 295, 350, and 370 mμ (ε = 8800, 34,000, 12,400, 1700, and 1700).

3 : 4 : 5 : 6-*Tetrahydro*-3-*hydroxy*-2-*methyl*-1-*azachrysene*.—The preceding base (0·605 g.) was reduced with sodium borohydride (0·25 g.) in boiling methanol (70 c.c.) for 20 min. Excess of borohydride was decomposed by dilute acetic acid, the solution was then basified and extracted with ether (4 × 30 c.c.). The ethereal solution was washed with brine, dried, and evaporated under reduced pressure. 3 : 4 : 5 : 6-*Tetrahydro*-3-*hydroxy*-2-*methyl*-1-*azachrysene* formed prisms (0·40 g.), m. p. 155—156°, from ethyl acetate (Found : C, 82·1; H, 6·5; N, 5·3. $C_{18}H_{17}ON$ requires C, 81·6; H, 6·3; N, 5·7%). Light absorption in MeOH : Max. 245, 270, 300, 317·5, 333, and 350 mμ (ε = 25,700, 27,000, 9250, 2000, 3500, and 3600).

2-*Methyl*-1-*azachrysene*.—The tetrahydro-compound (141 mg.) was heated with 30% palladised charcoal (24 mg.) at 260° for 25 min. The residue was extracted with boiling ethanol (25 c.c.) and ether (4 × 20 c.c.). The extracts were combined, dried, and evaporated under reduced pressure to a gum. Chromatography in light petroleum (b. p. 60—80°) on alumina gave 2-*methyl*-1-*azachrysene* obtained from the same solvent as irregular prisms (40 mg.), m. p. 115—116° (Ritchie, *J. Proc. Roy. Soc.*, *N.S.W.*, 1945, **78**, 186, gives m. p. 117°) (Found : C, 88·7; H, 5·4; N, 5·4. Calc. for $C_{18}H_{13}N$ : C, 88·9; H, 5·4; N, 5·8%). Light absorption in MeOH : Max. 225, 310, and 360 mμ (ε = 23,100, 5000, and 3000).

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