147. *New Syntheses of Heterocyclic Compounds. Part I. 2 : 3-Dialkylquinolines.*

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The reaction of anils, prepared by the condensation of the formyl derivatives of certain ketones with primary arylamines, with arylamine hydrochlorides leads under well-defined conditions to ring closure. The synthesis has been applied to the preparation in excellent yields of six types of heterocyclic systems. By selecting suitable derivatives of aniline, a large variety of substituted tetrahydroacridines has been obtained.

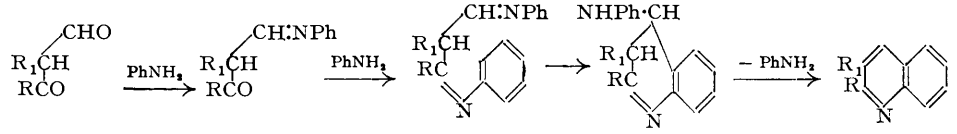
β-Diketones react with arylamines to give unsaturated products readily convertible into quinolines (Combes, *Compt. rend.*, 1887, **106**, 142). Substituted diketones behave in a similar way, Combes (*ibid.*, p. 1536) preparing 2 : 3 : 4-trimethylquinoline from methylacetylacetone. Borsche (*Ber.*, 1908, **41**, 2203) obtained a difficultly separable mixture of anilides from 1-acetyl*cyclo*hexan-2-one, which passed severally, on cyclisation, into 5-methyl-1 : 2 : 3 : 4-tetrahydroacridine and 10-methyl-1 : 2 : 3 : 4-tetrahydrophenanthridine. β-Keto-esters have also been used; Conrad and Limpach (*Ber.*, 1887, **20**, 944) obtained β-phenylaminocrotonic ester, which passed into 4-hydroxyquinaldine on dehydration, and substituted acetoacetic esters have been used by Dieckmann (*Annalen*, 1901, **317**, 91) and Sen and Basu (*J. Indian Chem. Soc.*, 1930, **7**, 435).

Attempts to carry out analogous condensations with β-keto-aldehydes have been only partially successful. Borsche (*Annalen*, 1910, **377**, 70) condensed formyl*cyclo*hexanone with aniline, but failed to cyclise the resulting 1-phenyliminomethyl*cyclo*hexan-2-one. Thielepape (*Ber.*, 1922, **55**, 127) attributed his lack of success with phenyliminomethylacetone (from formylacetone) to a *trans*-configuration of the anil. Romet (*Compt. rend.*, 1935, **200**, 1676) obtained a low yield of 3-methyl-2-ethylquinoline together with a smaller amount of the 3-methyl-4-ethyl isomeride from 2-phenyliminomethylpentan-3-one (from formyldiethyl ketone) by fusion with anhydrous zinc chloride, or by refluxing with this reagent in *iso*amyl-alcoholic solution. In an attempt to

develop this synthesis, 1-phenyliminomethyl*cyclo*hexan-2-one (Borsche, 1910, *loc. cit.*) was recovered unchanged after 10 hours' refluxing with the latter reagent. Considerable resinification occurred on fusion with anhydrous zinc chloride, but crude picrates were obtained in *ca.* 5% yield, so the synthesis resembles the production of acridine in 0·5% yield from salicylideneaniline by prolonged fusion with zinc chloride (Mohlau, *Ber.*, 1886, **19**, 2451). Sen-Gupta (J., 1915, **107**, 1347) prepared 3-cyano-2-ketohexahydroquinoline from formyl*cyclo*hexanone and cyanoacetamide. Basu (*Annalen*, 1934, **512**, 131) obtained ethyl 2-methyl-5 : 6 : 7 : 8-tetrahydroquinoline-3-carboxylate from formyl*cyclo*hexanone and ethyl β-aminocrotonate. Hydroxyquinolines have been prepared from formylacetic ester (Wislicenus, *Annalen*, 1917, **413**, 248) and from formylphenylacetic ester (Wislicenus and Erbe, *ibid.*, 1920, **421**, 146).

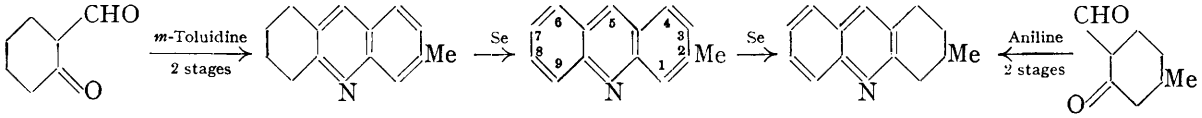
A new method whereby aliphatic β-keto-aldehydes, *i.e.*, the formyl (hydroxymethylene) derivatives of aliphatic ketones of the type $R{\cdot}CO{\cdot}CH_2R_1$ (where R and R_1 are alkyl groups), may be converted in *ca.* 50% yield into 2 : 3-dialkylquinolines consists in condensing the formyl derivative with the primary aromatic amine (1 mol.) to give quantitatively the anil $R{\cdot}CO{\cdot}CH(CH{:}NAr){\cdot}R_1$ and heating this product with the amine hydrochloride (1 mol.), either directly at 160—200° or in absolute alcoholic solution. The yield may be increased to 65% by using 2 mols. of the amine hydrochloride and 1 mol. of anhydrous zinc chloride to each mol. of the anil. The anils have in general been isolated, but this is not essential, as the crude condensation products may be used with equal success.

By analogy with salicylideneaniline, to which a *trans*-configuration has been assigned on the evidence of absorption spectra measurements (Hendricks, Wulf, Hilbert, and Liddel, *J. Amer. Chem. Soc.*, 1936, **58**, 1991), dipole moment measurements (de Gaouck and Le Fèvre, J., 1938, 741), and the formation of chelate metallic salts (Hunter and Marriott, J., 1937, 2000), it may be inferred that the anils derived from β-keto-aldehydes are similarly oriented. Their direct cyclisation is therefore improbable on stereochemical grounds. Again, direct cyclisation would give 3 : 4-dialkyl quinolines, whereas the 2 : 3-dialkyl isomerides are actually obtained (cf., however, Romet, *loc. cit.*). Intramolecular rearrangement of the anils would hardly take place in boiling alcoholic solution; production of the 2 : 3-dialkylquinolines therefore probably occurs as follows:



Systematic study has shown that the reaction is applicable not only to methyl ethyl ketone, but also to *cyclo*hexanone and its 3- and 4-methyl derivatives. A wide variety of substituted aniline derivatives has also been successfully used. 2 : 3-Dimethylquinoline, 2 : 3-dimethyl-7 : 8-benzoquinoline, and 2 : 3-*dimethyl*-5 : 6-*benzoquinoline* have been synthesised from formyl methyl ethyl ketone and aniline, 1-naphthylamine, and 2-naphthylamine respectively. The same amines and formyl*cyclo*hexanone yielded, by way of the corresponding anils, 1 : 2 : 3 : 4-tetrahydroacridine, 6 : 7 : 8 : 9-*tetrahydro*-1 : 2-*benzacridine*, and 6 : 7 : 8 : 9-tetrahydro-3 : 4-benzacridine respectively. The constitution of the last two compounds was established by dehydrogenation with selenium to 1 : 2-benzacridine and 3 : 4-benzacridine respectively.

An interesting feature of the synthesis is the apparent formation of only one isomeride from *m*-substituted anilines where two isomerides are theoretically to be expected. It has been possible to determine whether the methyltetrahydroacridine obtained from *m*-toluidine is the 6- or the 8-substituted derivative. The formyl derivative of 3-methyl*cyclo*hexanone (IV) (Wallach and Steindorff, *Annalen*, 1903, **329**, 109) was condensed with aniline to give 2-methyl-1 : 2 : 3 : 4-tetrahydroacridine (III), apparently identical with the compound obtained by Borsche (1910, *loc. cit.*) from 3-methyl*cyclo*hexanone by the isatin method. This base gave 2-methylacridine (V) on dehydrogenation with selenium, identical with the dehydrogenation product of the methyltetrahydroacridine obtained from formyl*cyclo*hexanone (I) and *m*-toluidine. This compound has therefore been assigned the constitution of 8-*methyl*-1 : 2 : 3 : 4-*tetrahydroacridine* (II).



(I.) (II.) (V.) (III.) (IV.)

Experimental.

Corrected m. p.'s given throughout. Microanalyses are by Mr. R. Maxim, University Chemical Laboratories, Cambridge.

Formyl*cyclo*hexanone was prepared essentially according to the directions of Borsche (1910, *loc. cit*): Sodium wire (23 g.), suspended in dry ether (500 ml.), was treated with a mixture of *cyclo*hexanone (110 ml.) and amyl formate (140 ml.), added dropwise under reflux during 1 hour with occasional shaking. After 12 hours the mixture was treated with 500 ml. of ice-water, the aqueous layer extracted with ether, and the formyl*cyclo*hexanone liberated from the sodium salt by acidification with cold dilute hydrochloric acid. It was extracted with ether and distilled, b. p. 86—88°/14 mm. Yield, 76 g.

Formyl methyl ethyl ketone (cf. Diels and Ilberg, *Ber.*, 1916, **49**, 158) was prepared by treating dry sodium ethoxide (from 10·6 g. of sodium), suspended in ether (330 ml.), at 0° with a mixture of methyl ethyl ketone (33 g.) and amyl

formate (54 g.). After 24 hours at 0° the sodium salt was collected, washed with ether, dried, and either used directly or dissolved in water and the formyl derivative liberated with ice-cold dilute sulphuric acid.

The anils were in general prepared by condensation of equivalent amounts of formyl methyl ethyl ketone or formyl-*cyclo*hexanone and the appropriate amine, both in alcoholic solution.

The following general procedure was used for the synthesis of the dialkylquinolines : The anil (1 mol.) in 10—20 vols. of absolute alcohol, amine hydrochloride (1 mol.), and anhydrous zinc chloride (1 mol.) were refluxed for 8—12 hours. The mixture was then made alkaline, and the basic portion extracted with ether. The dialkylquinoline was isolated from the residue left on removal of the ether by fractional ditillation under reduced pressure, or in a few cases as the picrate, and was purified by crystallisation from light petroleum or from aqueous acetone, yield, 50%. The picrates were all prepared in alcoholic solution and formed yellow crystals which were purified from nitrobenzene or from alcohol.

2 : 3-Dimethylquinoline, needles, m. p. 68—69° (Found : C, 84·3; H, 6·8; N, 9·2. Calc. : C, 84·1; H, 7·0; N, 8·9%) [picrate, m. p. 228—229° (decomp.) (Found : N, 14·5. Calc. : N, 14·5%)], was prepared from 3-(phenyliminomethyl)-butan-2-one (Diels and Ilberg, *Ber.*, 1916, **49**, 158). Pfitzinger (*J. pr. Chem.*, 1897, **56**, 315) gives m. p. 68—69° and 229° respectively.

2 : 3-*Dimethyl*-5 : 6-*benzoquinoline*, flat needles, m. p. 124—125° (Found : C, 86·7; H, 6·2; N, 7·0. $C_{15}H_{13}N$ requires C, 87·0; H, 6·3; N, 6·8%) [*picrate*, m. p. 260—261° decomp. (Found : N, 11·9. $C_{15}H_{13}N,C_6H_3O_7N_3$ requires N, 12·8%)], was prepared from 3-(*β-naphthyliminomethyl*)*butan*-2-*one*, pale yellow needles, m. p. 171—172° (Found : C, 79·9; H, 6·6; N, 6·2. $C_{15}H_{15}ON$ requires C, 80·0; H, 6·7; N, 6·2%). 2 : 3-Dimethyl-7 : 8-benzoquinoline, plates, m. p. 86—87° (Found : C, 86·8; H, 6·5; N, 7·0. Calc. : C, 87·0; H, 6·3; N, 6·8%) [picrate, m. p. 233·5° (decomp.) (Found : N, 12·5. Calc. : N, 12·8%)], was prepared from 3-(*α-naphthyliminomethyl*)*butan*-2-*one*, yellow needles, m. p. 110—111° (Found : C, 80·3; H, 6·8; N, 6·5. $C_{15}H_{15}ON$ requires C, 80·0; H, 6·7; N, 6·2%). Schenck and Bailey (*J. Amer. Chem. Soc.*, 1941, **63**, 2331) give m. p. 83—84° and 228—229° respectively.

1 : 2 : 3 : 4-Tetrahydroacridine formed prisms, m. p. 55—56° (Found : C, 85·0; H, 7·0; N, 7·9. Calc. : C, 85·2; H, 6·7; N, 7·7%), and its picrate had m. p. 222° (decomp.) (Found : N, 13·4. Calc. : N, 13·6%), neither depressed by authentic specimens prepared by Borsche's method (*Ber.*, 1908, **41**, 2203).

6 : 7 : 8 : 9-*Tetrahydro*-1 : 2-*benzacridine*, prisms, m. p. 96·5—97·5°, b. p. 254°/18 mm. (Found : C, 87·5; H, 6·6; N, 5·8. $C_{17}H_{15}N$ requires C, 87·6; H, 6·4; N, 6·0%) [*picrate*, m. p. 210·5—211·5° (decomp.) (Found : N, 12·4. $C_{17}H_{15}N,C_6H_3O_7N_3$ requires N, 12·1%)], was prepared from 1-(*α-naphthyliminomethyl*)cyclo*hexan*-2-*one*, orange crystals, m. p. 118—119° (Found : C, 80·8; H, 6·9; N, 5·6. $C_{17}H_{17}ON$ requires C, 81·2; H, 6·8; N, 5·6%). 1 : 2-Benzacridine, m. p. 108° (Found : C, 88·8; H, 5·0; N, 6·3. Calc. : C, 89·1; H, 4·8; N, 6·1%) [picrate, m. p. 229—230° (decomp.) (Found : N, 12·5. Calc. : N, 12·2%)], was obtained on dehydrogenation with selenium; Ullmann and Le Torre (*Ber.*, 1904, **37**, 2922) give m. p. 108° and 226—229° respectively. 6 : 7 : 8 : 9-Tetrahydro-3 : 4-benzacridine, plates, m. p. 115—116°, b. p. 260°/18 mm. (Found : C, 87·4; H, 6·6; N, 6·1. Calc. : C, 87·6; H, 6·4; N, 6·0%) [picrate, m. p. 219—220° (decomp.) (Found : N, 12·5. Calc. : N, 12·1%)], identical with the base, m. p. 114—115° (picrate, m. p. 218—219°), formulated by Kenner, Ritchie, and Wain (J., 1937, 1526) as tetrahydrobenzphenanthridine, was prepared from 1-(*β-naphthyliminomethyl*)cyclo*hexan*-2-*one*, pale yellow needles, m. p. 181—182° (Found : C, 81·1; H, 6·8; N, 5·8. $C_{17}H_{17}ON$ requires C, 81·2; H, 6·8; N, 5·6%). On dehydrogenation the base gave 3 : 4-benzacridine, m. p. 131° (Found : C, 89·2; H, 4·7; N, 6·2. Calc. : C, 89·1; H, 4·8; N, 6·1%) [picrate, m. p. 265—266° (decomp.) (Found : N, 12·4. Calc. : N, 12·2%)], not depressed by authentic specimens prepared by Ullmann's method (D.R.-P. 123,260).

9-*Methyl*-1 : 2 : 3 : 4-*tetrahydroacridine* formed octahedra, m. p. 77—78°, b. p. 190°/20 mm. (Found : C, 85·0; H, 7·5; N, 7·3. $C_{14}H_{15}N$ requires C, 85·3; H, 7·6; N, 7·1%); the *picrate* had m. p. 215—216° (decomp.) (Found : N, 13·0. $C_{14}H_{15}N,C_6H_3O_7N_3$ requires N, 13·1%). 8-*Methyl*-1 : 2 : 3 : 4-*tetrahydroacridine*, prismatic needles, m. p. 100—101°, b. p. 208°/25 mm. (Found : C, 85·6; H, 7·7; N, 7·4%) [*picrate*, m. p. 189—190° (decomp.) (Found : N, 12·8%)], was prepared from 1-(m-*tolyliminomethyl*)cyclo*hexan*-2-*one*, yellow needles, m. p. 152—153° (Found : C, 78·3; H, 8·2; N, 6·7. $C_{14}H_{17}ON$ requires C, 78·1; H, 7·9; N, 6·5%), and was dehydrogenated to 2-methylacridine, m. p. 129—130° (Found : C, 87·3; H, 6·0; N, 7·5. Calc. : C, 87·0; H, 5·7 : N, 7·3%) [*picrate*, m. p. 225—226° (decomp.) (Found : N, 13·0. $C_{14}H_{11}N,C_6H_3O_7N_3$ requires N, 13·3%)], for which Borsche (*Annalen*, 1910, **377**, 117) gives m. p. **125—126°**. 7-*Methyl*-1 : 2 : 3 : 4-*tetrahydroacridine*, octahedra, m. p. 61—62° (Found : C, 85·6; H, 7·7; N, 7·1%) [*picrate*, m. p. 189·5—190·5° (decomp.) (Found : N, 13·0%)], was prepared from 1-(p-*tolyliminomethyl*)cyclo*hexan*-2-*one*, feathery yellow crystals, m. p. 163—164° (Found : C, 78·4; H, 8·1; N, 6·7%). 2-Methyl-1 : 2 : 3 : 4-tetrahydroacridine, octahedra, m. p. 76—77°, b. p. 195°/15 mm. (Found : C, 85·2; H, 7·6; N, 7·5%) [*picrate*, m. p. 184—185° (decomp.) (Found : N, 12·3%)], was dehydrogenated to 2-methylacridine, m. p. 129—130° (Found : C, 87·1; H, 6·0; N, 7·3%) [picrate, m. p. 225—226° (decomp.) (Found : N, 13·4%)]. Both base and picrate are identical with the compounds described under 8-methyl-1 : 2 : 3 : 4-tetrahydroacridine. 3-Methyl-1 : 2 : 3 : 4-tetrahydroacridine, octahedra, m. p. 87—88°, b. p. 180°/15 mm. (Found : C, 85·2; H, 7·4; N, 7·3%) [picrate, m. p. 199—200° (decomp.) (Found : N, 12·8%)], was prepared from 1-(*phenyliminomethyl*)-4-*methyl*cyclo*hexan*-2-*one*, orange-yellow plates, m. p. 161—162° (Found : C, 78·0; H, 7·8; N, 6·8. $C_{14}H_{17}ON$ requires C, 78·1; H, 7·9; N, 6·5%); Borsche (*loc. cit.*) gives m. p. 84—85° and 194—195° respectively.

6 : 9-*Dimethyl*-1 : 2 : 3 : 4-*tetrahydroacridine*, prisms, m. p. 38—39° (Found : C, 85·5; H, 8·3; N, 6·7. $C_{15}H_{17}N$ requires C, 85·3; H, 8·1; N, 6·6%) [*picrate*, m. p. 187—188° (decomp.) (Found : N, 12·4. $C_{15}H_{17}N,C_6H_3O_7N_3$ requires N, 12·7%)], was prepared from 1-p-*xylyliminomethyl*)cyclo*hexan*-2-*one*, orange-yellow plates, m. p. 100—101° (Found : C, 78·3; H, 8·1; N, 6·5. $C_{15}H_{19}ON$ requires C, 78·6; H, 8·3; N, 6·1%).

7-*Phenyl*-1 : 2 : 3 : 4-*tetrahydroacridine*, needles, m. p. 130° (Found : C, 88·3; H, 6·7; N, 5·5. $C_{19}H_{17}N$ requires C, 88·0; H, 6·6; N, 5·4%) [*picrate*, m. p. 246—247° (decomp.) (Found : N, 11·3. $C_{19}H_{17}N,C_6H_3O_7N_3$ requires N, 11·5%)], was prepared from 1-(*diphenylyl-4'-iminomethyl*)cyclo*hexan*-2-*one*, yellow needles, m. p. 201—202° (Found : C, 82·2; H, 7·0; N, 5·2. $C_{19}H_{19}ON$ requires C, 82·3; H, 6·9; N, 5·1%). It was dehydrogenated to 3-*phenylacridine*, plates, m. p. 127—128° (Found : C, 89·3; H, 5·4; N, 5·6. $C_{19}H_{13}N$ requires C, 89·4; H, 5·1; N, 5·5%), of which the *picrate* had m. p. 244—245° (decomp.) (Found : N, 11·5. $C_{19}H_{13}N,C_6H_3O_7N_3$ requires N, 11·6%).

9-*Chloro*-1 : 2 : 3 : 4-*tetrahydroacridine* formed octahedra, m. p. 94·5—95·5°, b. p. 220°/20 mm. (Found : C, 71·4; H, 5·8; N, 6·6. $C_{13}H_{12}NCl$ requires C, 71·7; H, 5·5; N, 6·4%); the *picrate* had m. p. 197—198° (decomp.) (Found : N, 12·6. $C_{13}H_{12}NCl,C_6H_3O_7N_3$ requires N, 12·8%). 6(or 8)-*Chloro*-1 : 2 : 3 : 4-*tetrahydroacridine*, octahedra, m. p. 92°, b. p. 202—203°/15 mm. (Found : C, 71·3; H, 5·6; N, 6·8%) [*picrate*, m. p. 204—205° (decomp.) (Found : N, 12·6%)], was prepared from 1-(m-*chlorophenyliminomethyl*)cyclo*hexan*-2-*one*, lemon-yellow needles, m. p. 148—150° (Found : C, 66·9; H, 6·3; N, 6·3. $C_{13}H_{14}ONCl$ requires C, 66·4; H, 6·0; N, 6·0%). 7-*Chloro*-1 : 2 : 3 : 4-*tetrahydroacridine*, flat needles, m. p. 95—96°, b. p. 212—214°/20 mm. (Found : C, 72·0; H, 5·6; N, 6·6%) [*picrate*, m. p. 188—189° (decomp.). (Found : N, 12·8%)], was prepared from 1-(p-*chlorophenyliminomethyl*)cyclo*hexan*-2-*one*, lemon-yellow octahedra, m. p. 169—170° (Found : C, 66·3; H, 5·8; N, 6·2%).

9-*Bromo*-1 : 2 : 3 : 4-*tetrahydroacridine* formed octahedra, m. p. 79—80°, b. p. 227—228°/15 mm. (Found : C, 59·3; H, 4·8; N, 5·4. $C_{13}H_{12}NBr$ requires C, 59·5; H, 4·6; N, 5·3%) [*picrate*, m. p. 191—192° (decomp.) (Found : N, 11·4. $C_{13}H_{12}NBr,C_6H_3O_7N_3$ requires N, 11·1%)]. 6(or 8)-*Bromo*-1 : 2 : 3 : 4-*tetrahydroacridine*, needles, m. p. 86—87°, b. p. 217—218°/15 mm. (Found : C, 59·7; H, 4·7; N, 5·4%) [*picrate*, m. p. 213·5—214·5° (decomp.) (Found : N, 11·5%)],

was prepared from 1-(m-*bromophenyliminomethyl*)cyclo*hexan*-2-*one*, lemon-yellow plates, m. p. 155—156° (Found: C, 55·3; H, 5·3; N, 5·3. $C_{13}H_{14}ONBr$ requires C, 55·7; H, 5·0; N, 5·0%). 7-Bromo-1 : 2 : 3 : 4-tetrahydroacridine, octahedra, m. p. 93—94°, b. p. 223—224°/18 mm. (Found: C, 59·6; H, 4·8; N, 5·4%) [picrate, m. p. 213·5—214·5° (decomp.) (Found: N, 11·4%)], was prepared from 1-(p-*bromophenyliminomethyl*)cyclo*hexan*-2-*one*, corn-coloured plates, m. p. 175—176° (Found: C, 55·7; H, 5·2; N, 5·3%); Borsche (*loc. cit.*) gives m. p. 94° and 195° respectively.

7-*Iodo*-1 : 2 : 3 : 4-*tetrahydroacridine* (4 hrs. refluxing, no zinc chloride), squat rods, m. p. 86·5—87·5° (Found: C, 50·5; H, 4·2; N, 4·6. $C_{13}H_{12}NI$ requires C, 50·5; H, 3·9; N, 4·5%) [*picrate*, m. p. 219·5—220·5° (decomp.) (Found: N, 10·1. $C_{13}H_{12}NI,C_6H_3O_7N_3$ requires N, 10·4%)], was prepared from 1-(p-*iodophenyliminomethyl*)cyclo*hexan*-2-*one*, lemon-yellow needles, m. p. 168—169° (Found: C, 47·9; H, 4·3; N, 4·6. $C_{13}H_{14}ONI$ requires C, 47·7; H, 4·3; N, 4·3%).

6(or 8)-*Carbethoxy*-1 : 2 : 3 : 4-*tetrahydroacridine*, needles, m. p. 63—64° (Found: C, 75·3; H, 6·5; N, 5·5. $C_{16}H_{17}O_2N$ requires C, 75·3; H, 6·7; N, 5·5%) [*picrate*, m. p. 161° (decomp.) (Found: N, 11·0. $C_{16}H_{17}O_2N,C_6H_3O_7N_3$ requires N, 11·1%)], was prepared from 1-(m-*carbethoxyphenyliminomethyl*)cyclo*hexan*-2-*one*, flat yellow needles, m. p. 143—144° (Found: C, 70·0; H, 7·2; N, 5·4. $C_{16}H_{19}O_3N$ requires C, 70·3; H, 7·0; N, 5·1%). 7-*Carbethoxy*-1 : 2 : 3 : 4-*tetrahydroacridine*, prismatic needles, m. p. 94·5—95·5°, b. p. 234°/20 mm. (Found: C, 75·4; H, 6·7; N, 5·8%) [*picrate*, m. p. 197—198° (decomp.) (Found: N, 11·0%)], was prepared from 1-(p-*carbethoxyphenyliminomethyl*)cyclo*hexan*-2-*one*, feathery yellow needles, m. p. 181—182° (Found: C, 70·6; H, 7·0; N, 5·3%). It was hydrolysed to 1 : 2 : 3 : 4-*tetrahydroacridine*-7-*carboxylic acid*, needles, m. p. 290—291° (Found: C, 74·4; H, 5·7; N, 6·4. $C_{14}H_{13}O_2N$ requires C, 74·0; H, 5·7; N, 6·1%). Acridine derivatives could not be obtained from 1-(o-*carboxyphenyliminomethyl*)cyclo*hexan*-2-*one*, orange-yellow needles, m. p. 199—200° (Found: C, 68·8; H, 6·0; N, 5·4. $C_{14}H_{15}O_3N$ requires C, 68·5; H, 6·1; N, 5·7%), and from 1-(o-*carbomethoxyphenyliminomethyl*)cyclo*hexan*-2-*one*, needles, m. p. 134·5—135·5° (Found: C, 69·6; H, 6·3; N, 5·6. $C_{15}H_{17}O_3N$ requires C, 69·5; H, 6·6; N, 5·4%).

7-*Hydroxy*-1 : 2 : 3 : 4-*tetrahydroacridine*, plates, m. p. 290—291° (Found: C, 78·8; H, 6·7; N, 7·4. $C_{13}H_{13}ON$ requires C, 78·4; H, 6·5; N, 7·0%) [*picrate*, m. p. 229·5—230·5° (decomp.) (Found: N, 12·5. $C_{13}H_{13}ON,C_6H_3O_7N_3$ requires N, 13·1%)], was prepared from 1-(p-*hydroxyphenyliminomethyl*)cyclo*hexan*-2-*one*, golden-yellow plates, m. p. 154—155° (Found: C, 71·7; H, 7·0; N, 6·7. $C_{13}H_{15}O_2N$ requires C, 71·9; H, 6·9; N, 6·5%).

7-*Nitro*-1 : 2 : 3 : 4-*tetrahydroacridine*.—1-(p-*Nitrophenyliminomethyl*)cyclo*hexan*-2-*one* (40 g.), yellow needles, m. p. 244—245° (Found: C, 63·4; H, 5·9; N, 11·5. $C_{13}H_{14}O_3N_2$ requires C, 63·4; H, 5·7; N, 11·4%), was treated as above, and the mixture poured into excess of sodium carbonate solution and extracted with benzene (1000 ml.). The product in dry benzene (300 ml.) was refluxed for 30 minutes with acetic anhydride (50 ml.), water added (700 ml.), and the *p*-nitroacetanilide collected after 12 hours and washed three times with benzene (100 ml.). The acetic acid layer was removed, and the benzene washed with small volumes of dilute hydrochloric acid (total, 2 l. containing 700 ml. of concentrated acid). The acetic acid and the hydrochloric acid liquors were bulked and made alkaline with ammonia; the precipitated 7-*nitro*-1 : 2 : 3 : 4-*tetrahydroacridine* crystallised from acetone (norit) in needles (15 g.), m. p. 170·5—171·5° (Found: C, 68·6; H, 5·3; N, 12·5. $C_{13}H_{12}O_2N_2$ requires C, 68·4; H, 5·3; N, 12·3%). The *picrate* had m. p. 204·5° (decomp.) (Found: N, 14·9. $C_{13}H_{12}O_2N_2,C_6H_3O_7N_3$ requires N, 15·3%).

On reduction 7-*amino*-1 : 2 : 3 : 4-*tetrahydroacridine* was obtained; it formed rods, m. p. 141° (Found: C, 79·0; H, 7·2; N, 14·4. $C_{13}H_{14}N_2$ requires C, 78·8; H, 7·1; N, 14·4%), and gave an *acetyl* derivative crystallising in needles, m. p. 218·5—219·5° (Found: C, 75·1; H, 7·0; N, 11·9. $C_{15}H_{16}ON_2$ requires C, 75·0; H, 6·7; N, 11·7%). An acridine derivative could not be obtained from 1-(m-*nitrophenyliminomethyl*)cyclo*hexan*-2-*one*, orange needles, m. p. 171—172° (Found: C, 63·4; H, 6·0; N, 11·6%).

9-*Methoxy*-1 : 2 : 3 : 4-*tetrahydroacridine*, octahedra, m. p. 121·5—122·5°, b. p. 212°/20 mm. (Found: C, 79·0; H, 7·1; N, 7·0. $C_{14}H_{15}ON$ requires C, 78·9; H, 7·0; N 6·6%) [*picrate*, m. p. 206·5—207·5° (decomp.) (Found: N, 12·7. $C_{14}H_{15}ON,C_6H_3O_7N_3$ requires N, 12·7%)], was prepared from 1-(o-*methoxyphenyliminomethyl*)cyclo*hexan*-2-*one*, feathery yellow needles, m. p. 131—132° (Found: C, 72·8; H, 7·6; N, 6·2. $C_{14}H_{17}O_2N$ requires C, 72·7; H, 7·4; N, 6·1%). 7-*Methoxy*-1 : 2 : 3 : 4-*tetrahydroacridine*, octahedra, m. p. 90—91°, b. p. 223°/15 mm. (Found: C, 79·1; H, 7·3; N, 6·7%) [*picrate*, m. p. 223·5—224·5° (decomp.) (Found: N, 11·7%)], was prepared from 1-(p-*methoxyphenyliminomethyl*)cyclo*hexan*-2-*one*, pale yellow needles, m. p. 149—150° (Found: C, 72·9; H, 7·6; N, 6·3%).

6(or 8)-*Acetyl*-1 : 2 : 3 : 4-*tetrahydroacridine*, flat needles, m. p. 131—132° (Found: C, 79·9; H, 6·5; N, 6·2. $C_{15}H_{15}ON$ requires C, 80·0; H, 6·7; N, 6·2%) [*picrate*, m. p. 211—212° (decomp.) (Found: N, 11·8. $C_{15}H_{15}ON,C_6H_3O_7N_3$ requires N, 12·3%)], was prepared from 1-(m-*acetylphenyliminomethyl*)cyclo*hexan*-2-*one*, feathery yellow crystals, m. p. 139—140° (Found: C, 74·0; H, 7·3; N, 6·0. $C_{15}H_{17}O_2N$ requires C, 74·1; H, 7·0; N, 5·8%).

7-*Phenylamino*-1 : 2 : 3 : 4-*tetrahydroacridine*, golden-yellow needles, m. p. 173°, b. p. 290°/15 mm. (Found: C, 83·1; H, 6·9; N, 10·2. $C_{19}H_{18}N_2$ requires C, 83·2; H, 6·6; N, 10·2%) [*picrate*, orange-brown needles, m. p. 251—252° (decomp.) (Found: N, 13·7. $C_{19}H_{18}N_2,C_6H_3O_7N_3$ requires N, 13·9%)], was prepared from 1-(p-*phenylaminophenyliminomethyl*)cyclo*hexan*-2-*one*, golden-yellow plates, m. p. 144—145° (Found: C, 78·6; H, 7·4; N, 10·0. $C_{19}H_{20}ON_2$ requires C, 78·1; H, 6·9; N, 9·6%).

Quinoline derivatives could not be obtained from the formyl derivatives of the following ketones: Acetophenone, propiophenone, benzyl methyl ketone, phenyl benzyl ketone, *cyclo*pentanone, *i*-menthone, 2-methyl*cyclo*hexanone, α-tetralone, and acetoacetic ester. 2-Hydroxy-1-naphthaldehyde anil was recovered unchanged.

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