397. *The Nuclear Alkylation of Aromatic Bases. Part III. The Action of Methyl Alcohol on the Hydrochlorides of α- and β-Naphthylamine.*

By Donald H. Hey and E. R. Buckley Jackson.

The nuclear alkylation of bases of the benzene series by the action of an aliphatic alcohol on a salt of the base at an elevated temperature has been studied by many workers (for references see Hey, Part I, J., 1931, 1581), but the application of the reaction to bases of polycyclic aromatic systems has received little attention (compare Hey and Jackson, Part II, J., 1934, 645). The action of methyl alcohol on α-naphthylamine hydrochloride at 180° gave rise mainly to dimethyl-α-naphthylamine and α-naphthol (Hantzsch, *Ber.*, 1880, **13**, 1347; Pinnow, *Ber.*, 1899, **32**, 1405; Gokhlé and Mason, J., 1930, 1757), and Pinnow (*loc. cit.*), using β-naphthylamine hydrochloride, obtained only dimethyl-β-naphthylamine and β-naphthyltrimethylammonium chloride. The reaction involving the rearrangement on heating of an alkylarylamine hydrochloride was applied by Heap (J., 1933, 495) to *iso*propyl-β-naphthylamine hydrochloride in an unsuccessful attempt to obtain 1-*iso*-propyl-β-naphthylamine. Thus there appears to be no recorded example of nuclear alkylation in the naphthalene series, either by the action of an aliphatic alcohol on a naphthylamine hydrochloride (see, however, Landshoff, *Ber.*, 1878, **11**, 638) or by any modification of this reaction.

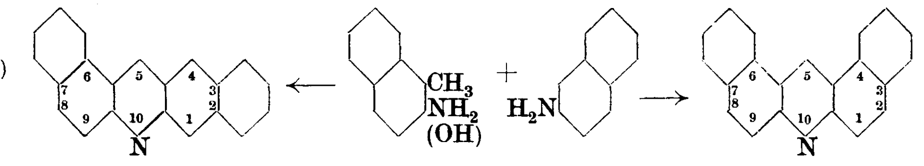
The main factor governing nuclear methylation (*C*-methylation), which is preceded by *N*-methylation, is probably temperature, and, since previous workers in the naphthalene series had obtained *N*-methylated bases only, it seemed likely that the critical temperature for " migration " had not been reached. In the present work the reaction temperatures were somewhat higher than those used by previous workers in this series and varied from 200° to 250°. Dziewonski and Dragan (*Bull. Acad. Polonaise*, 1934, *A*, 398) obtained 1-methyl-2-naphthol by heating dimethylaniline and β-naphthol at 300° in the presence of a trace of sodium β-naphthoxide.

The action of methyl alcohol (3 mols.) on α-naphthylamine hydrochloride in an autoclave at 240—250° is now shown to give mainly α-naphthol and tarry matter; at a slightly lower temperature (220°) dimethyl-α-naphthylamine also is produced. With methyl alcohol (4 mols.) at 230—250°, the amount of tarry matter formed is reduced and the product consists of α-naphthol together with smaller quantities of 2-methyl-1-naphthol, α-naphthylamine, methyl-α-naphthylamine, and α-methoxynaphthalene. Nuclear methylation is thus effected, but the extent to which it occurs appears to be limited.

In contrast with the behaviour of α-naphthylamine hydrochloride, the action of methyl alcohol (3 mols.) on β-naphthylamine hydrochloride at 200—220° gives a mixture containing dimethyl-β-naphthylamine, di-β-naphthylamine, β-naphthol, β-methoxynaphthalene, and bases of the dibenzacridine series, whereas with methyl alcohol (4 mols.) at 240—250° the entry of a methyl group into the nucleus is readily effected and the product consists largely of 1-methyl-2-naphthol and methylamine hydrochloride together with smaller quantities of dimethyl-β-naphthylamine, di-β-naphthylamine, β-methoxynaphthalene, and dibenzacridines. Nuclear methylation thus takes place far more readily in the β-naphthylamine series than in the α-series and the product is not a base but a phenol.

The bases of the dibenzacridine series formed in the above reactions were characterised by the ready formation of sparingly soluble hydrochlorides. The two pure compounds isolated have been identified as 3 : 4 : 6 : 7-dibenzacridine (I), which forms the greater part of the mixture, and 2 : 3 : 6 : 7-dibenzacridine (II). The formation of acridine derivatives in similar reactions in the benzene series has been recorded by Liebermann and Kardos (*Ber.*, 1913, **46**, 207; 1914, **47**, 1563) and Hey (Part I, *loc. cit.*). The almost exclusive formation of 1 : 3 : 7 : 9-tetramethylacridine during the methylation of *o*- or *p*-toluidine (Part I, *loc. cit.*) indicates that the formation of an acridine derivative in these reactions probably involves the interaction of either the amino-groups of two molecules, with elimination of ammonia (or its methyl derivatives), or an amino-group of one molecule and a hydroxyl group of another, with elimination of water. In this manner β-naphthylamine can give rise, theoretically, to 2 : 3 : 6 : 7-, 2 : 3 : 7 : 8-, and 3 : 4 : 6 : 7-dibenzacridine. Of these, the most probable is 3 : 4 : 6 : 7-dibenzacridine (I), in which the *meso*-carbon atom bridges the more reactive α-positions of the original naphthalenic structures. The formation of 2 : 3 : 6 : 7-dibenzacridine (II) involves a carbon bridge between an α- and a β-position, and in the case of the linear 2 : 3 : 7 : 8-dibenzacridine two β-positions are involved. Previous workers have repeatedly shown that, normally, the β-carbon atoms in naphthalene are less prone to take part in ring formation than the α-atoms (Skraup and Cobenzl, *Monatsh.*, 1883, **4**, 438; Lellmann and Schmidt, *Ber.*, 1887, **20**, 3154; Morgan, J., 1898, **73**, 536; 1900, **77**, 814; Strohbach, *Ber.*, 1901, **34**, 4146; Bacovescu, *Ber.*, 1910, **43**, 1280; Dey, Rau, and Sankaranarayanan, *J. Indian Chem. Soc.*, 1932, **9**, 71; Dey and Lakshminarayanan, *ibid.*, p. 149; Chakravarti, *ibid.*, p. 389. Compare also v. Braun and Gruber, *Ber.*, 1922, **55**, 1710; Cook, J., 1931, 2524; Hewett, this vol., p. 596). The proportion in which the two dibenzacridines were isolated, together with the failure to detect 2 : 3 : 7 : 8-dibenzacridine in the product, is in general agreement with these observations.

(II.)



(I.)

In the corresponding reaction with α-naphthylamine hydrochloride the absence of any definite indication of dibenzacridine formation is not surprising, since only one dibenzacridine could be formed on the lines indicated above, namely, 1 : 2 : 8 : 9-dibenzacridine, and its formation would involve a carbon bridge between two β-positions of the original naphthalene nuclei.

The two series of experiments also differed in that there was a far greater tendency for the formation of tarry matter in the α- than in the β-naphthylamine series. Similar contrasting behaviour has been noted elsewhere by Benz (*Ber.*, 1883, **16**, 8) and Merz and Weith (*Ber.*, 1881, **14**, 2343).

The formation of naphthyl methyl ethers probably results from the direct methylation of the naphthols (cf. Hantzsch, *loc. cit.*), the production of which in appreciable quantity is to be expected in view of the well-known mobility of the amino-group in the naphthalene series (compare also Part I, *loc. cit.*). The possibility that the methylnaphthols are formed by molecular rearrangement of the naphthyl methyl ethers is highly improbable : reactions of this type with phenolic ethers of simple normal alcohols do not appear to be known (cf. Niederl and Natelson, *J. Amer. Chem. Soc.*, 1932, **54**, 1063).

The comparative yields of naphthol were greater in the experiments with α-naphthylamine than in those with β-naphthylamine and it thus appeared possible that the hydrolysis of dimethyl-α-naphthylamine under the conditions of experiment is so facile that the process whereby nuclear methylation is effected cannot proceed to any appreciable extent. In order to diminish this hydrolysis dimethyl-α-naphthylamine hydrochloride was heated with methyl alcohol (1½ mols.) : the formation of water which occurs during the preliminary methylation of the primary base thus being circumvented, it was anticipated that conditions might now be more favourable for the entry of a methyl group into the nucleus by " migration." The main products, however, were α-naphthol and methyl-α-naphthylamine together with some tarry matter. The formation of the secondary base probably results from the separation of methyl chloride from the hydrochloride of the tertiary base, thus : $\alpha\text{-}C_{10}H_7\cdot NMe_2,HCl \longrightarrow \alpha\text{-}C_{10}H_7\cdot NHMe + MeCl$ (cf. Hickinbottom and Ryder, J., 1931, 1281). In addition, it may be noted that in the experimental work on β-naphthylamine hydrochloride the volatile base isolated from the product is methylamine, and not dimethylamine, thus :

$$\beta\text{-}C_{10}H_7\cdot NMe_2,HCl \longrightarrow C_{10}H_6Me\cdot NHMe,HCl \xrightarrow{H_2O} C_{10}H_6Me\cdot OH + NH_2Me,HCl$$

The formation of a diarylamine by the action of methyl alcohol on an amine hydrochloride was observed in the diphenyl series (Part II, *loc. cit.*). It is known that diarylamines may readily be formed in the naphthalene series (Landshoff, *loc. cit.*; Benz, *loc. cit.*; Klopsch, *Ber.*, 1885, **18**, 1585; Heap, *loc. cit.*). The isolation of di-β-naphthylamine in the present work is therefore not surprising, but it was not possible to isolate any di-α-naphthylamine (cf. Benz, *loc. cit.*).

EXPERIMENTAL.

In the following experiments an electrically heated Monel metal autoclave of 250 c.c. capacity was used, the reaction mixture being contained in a close-fitting open Pyrex vessel within the autoclave (cf. Parts I and II, *locc. cit.*).

Action of Methyl Alcohol on α-Naphthylamine Hydrochloride.—(A) *With* 3 *mols. of methyl alcohol.* (i) α-Naphthylamine hydrochloride (50 g.) and methyl alcohol (27 g.) were heated at 240—250° for 12 hours. The dark viscous product was extracted from the autoclave by successive treatments with 50% sulphuric acid, hot water, and aqueous sodium hydroxide. The total extract was made strongly acid and steam-distilled, the distillate extracted with benzene, and this extract dried (sodium sulphate) and evaporated. The residual oil, on distillation, yielded three fractions : (a) b. p. 260—280° (0·5 g.), (b) b. p. 280—290° (5 g.), and (c) b. p. 290—330° (1 g.). Solid material separated from fractions (a) and (b) and trituration with light petroleum (b. p. 40—60°), followed by crystallisation from that solvent, gave α-naphthol in fine white needles, m. p. 93—94°, not depressed by an authentic specimen. A small quantity of α-naphthol was also extracted from fraction (c) by means of aqueous alkali. The non-crystallisable portion of fractions (a) and (b) was a red oil of pleasant odour (1 g.), insoluble in acids and alkalis, and probably consisted of α-methoxynaphthalene.

The residue from the steam distillation was made strongly alkaline with aqueous sodium hydroxide; a powerful ammoniacal odour was liberated, and some metallic hydroxide precipitated. Benzene extracted from the mixture a tarry material (20 g.) containing only a small quantity of basic material.

(ii) In an attempt to reduce the amount of tarry matter formed, a second experiment was carried out with the same quantities of reactants but at 220°. The product was treated as described above. After the steam distillation, however, tarry matter, similar to, but less in quantity than, that described above, was separated from the acid solution by decantation prior to the addition of alkali. The oil from the steam distillate (12 g.) solidified and after crystallisation from light petroleum (b. p. 40—60°) α-naphthol was obtained in white needles, m. p. and mixed m. p. 93—94° (picrate, m. p. 191°). The light petroleum mother-liquors were evaporated : the residual oil (1·5 g.), freed from traces of α-naphthol by washing with aqueous alkali, behaved similarly to the neutral product isolated in experiment A (i).

Evaporation of the benzene extract from the alkaline solution yielded a residue (8 g.), which distilled as a pale yellow oil at 275—295°. The oil was unaffected by boiling acetic anhydride, but readily yielded a picrate in alcoholic solution. Crystallisation from absolute alcohol gave small yellow needles, m. p. 142—143°, not depressed by the picrate (m. p. 144°) of dimethyl-α-naphthylamine, prepared from α-naphthylamine and methyl sulphate as described by Gokhlé and Mason (*loc. cit.*). This preparation also yielded some secondary base, which was isolated as acetomethyl-α-naphthalide in needles, m. p. 96—97°. Landshoff (*loc. cit.*) gives m. p. 90—91° and Rodionow and Vvedenskij (*Bull. Soc. chim.*, 1929, **45**, 122) give m. p. 93—94°.

(B) *With* 4 *mols. of methyl alcohol.* α-Naphthylamine hydrochloride (50 g.) and methyl alcohol (36 g.) were heated at 230—250° for 12 hours. The product was extracted from the autoclave successively with hot benzene, concentrated hydrochloric acid, and aqueous sodium hydroxide. The whole was shaken, with the addition of more benzene and hydrochloric acid, and the benzene layer was separated (aqueous acid extract = X) and shaken with aqueous sodium hydroxide (aqueous alkaline extract = Y; residual benzene solution = Z).

The aqueous acid extract (X) was filtered, made alkaline, filtered from precipitated metallic hydroxides, and extracted with benzene. Evaporation of the solvent left a dark oil (4 g.), b. p. 285—295°, which was treated with acetic anhydride and distilled. Two fractions were collected, (a) b. p. 290—310° and (b) b. p. > 310°. Fraction (b) solidified and yielded aceto-α-naphthalide (m. p. and mixed m. p. 157—158°) after crystallisation from dilute alcohol. Fraction (a) partly solidified on trituration with light petroleum and consisted of a mixture of aceto-α-naphthalide and acetomethyl-α-naphthalide.

The aqueous alkaline extract (Y) was acidified and extracted with benzene. After filtration and removal of solvent, the residue distilled as a red oil (8 g.), b. p. 290—300°, which solidified when cold. Crystallisation from light petroleum (b. p. 40—60°) yielded α-naphthol (m. p. and mixed m. p. 93—94°) and, after the separation of further batches of α-naphthol from the mother-liquor, a product was obtained, m. p. 55—58°. Further crystallisation from the same solvent and treatment with charcoal raised the m. p. to 62—63° and a mixed m. p. with α-naphthol showed a marked depression. The compound, obtained in soft white needles, is therefore regarded as 2-methyl-1-naphthol (Found : C, 83·1; H, 6·6. Calc. for $C_{11}H_{10}O$: C, 83·5; H, 6·3%). Lesser (*Annalen*, 1914, **402**, 42) records m. p. 61° and Veselý and Páč (*Chem. Zentr.*, 1930, II, 1547) m. p. 64—65°.

The residual benzene solution (Z), containing neutral or weakly basic products, was dried over sodium sulphate and distilled. After removal of solvent, three fractions were collected, (a) b. p. 250—300° (1·5 g.), (b) b. p. 300—350° (1·0 g.), and (c) b. p. > 350° (7·0 g.), leaving a residue of tar. Fraction (a) was dissolved in ether, washed successively with aqueous acid and aqueous alkali, dried, and distilled. A yellow neutral oil was obtained, b. p. 260—270°, similar to that isolated from the steam distillate in experiments A (i) and A (ii). Admixture with 1 : 3 : 5-trinitrobenzene in hot alcoholic solution yielded the addition compound of α-methoxynaphthalene in yellow needles, m. p. 139—140° (Sudborough and Beard, J., 1911, **99**, 214, record m. p. 137—138°). Fractions (b) and (c) became very dark on standing and neither reacted with acetic anhydride nor united with picric acid.

This method of working up the products of reaction is more effective than prolonged steam-distillation, as employed in experiments A (i) and A (ii), which may bring about an increase in the amount of tarry matter.

Action of Methyl Alcohol on Dimethyl-α-naphthylamine Hydrochloride.—(C) The hydrochloride of dimethyl-α-naphthylamine (40 g.; 1 mol.) (obtained quantitatively as a deliquescent white powder by the passage of a rapid stream of dry hydrogen chloride into a dry ethereal solution of the base) and methyl alcohol (9 g.; 1·5 mols.) were heated at 230—250° for 12 hours. The product, a brown syrup of pronounced ammoniacal and fishy odour, was treated as described in experiments A (i) and (ii). The benzene extract of the steam distillate was dried and evaporated. The residual oil (5 g.) solidified and crystallisation from light petroleum (b. p. 40—60°) yielded α-naphthol (m. p. and mixed m. p. 93—94°). Evaporation of the mother-liquor yielded a small quantity of a neutral oil, similar to that obtained in the previous experiments and probably consisting of α-methoxynaphthalene.

The residue from the steam distillation was decanted from insoluble tarry material (similar to that described above), made alkaline, and extracted with benzene. The extract was dried over potassium carbonate and evaporated. The residue distilled as a pale yellow oil (7 g.), b. p. 270—295°, which was boiled under reflux for 1 hour with an excess of acetic anhydride. After removal of the excess of acetic anhydride by evaporation the residue, which solidified, was crystallised from light petroleum (b. p. 40—60°), acetomethyl-α-naphthalide being obtained in small white needles, m. p. and mixed m. p. 95—96°.

Action of Methyl Alcohol on β-Naphthylamine Hydrochloride.—(D) *With* 3 *mols. of methyl alcohol.* β-Naphthylamine hydrochloride (50 g.) and methyl alcohol (27 g.) were heated at 200—220° for 12 hours. The product was removed from the autoclave with the aid of benzene (500 c.c.), and the solution shaken with 10% aqueous sodium hydroxide (500 c.c.). An ammoniacal fishy odour was liberated, and metallic hydroxide precipitated. After separation of the filtered aqueous alkaline layer (U) the residual benzene solution was washed with water and shaken vigorously with 15% hydrochloric acid (500 c.c.), a yellow hydrochloride being precipitated. The filtered aqueous acid extract (V) was separated from the benzene layer (W).

The aqueous alkaline solution (U) was acidified, and the resulting mixture of solution and precipitated solid extracted with ether. The extract, dried over sodium sulphate, was evaporated; the residual oil (5 g.) solidified when cold. Two crystallisations from light petroleum (b. p. 60—80°) yielded β-naphthol in white needles, m. p. and mixed m. p. 119—120° (picrate, m. p. and mixed m. p. 155°).

The yellow hydrochloride (above) was suspended in hot water and treated with an excess of aqueous sodium hydroxide. The liberated base (3 g.) was washed with water and dried. Fractional crystallisation from benzene–light petroleum (b. p. 60—80°) yielded mainly 3 : 4 : 6 : 7-dibenzacridine in pale yellow leaflets, m. p. 208—210°, and a second compound in white needles, m. p. 145—148°, the further purification of which was impracticable owing to the small quantity available. A mixed m. p. of the 3 : 4 : 6 : 7-dibenzacridine with an authentic specimen showed no depression (see also experiment E).

The aqueous acid extract (V), made alkaline with aqueous sodium hydroxide, evolved an ammoniacal fishy odour and liberated an oil, which was extracted with benzene. The solvent was evaporated from the dried extract (potassium carbonate), and the residual oil distilled, giving fractions (a) b. p. 305—310° (9 g.) and (b) b. p. 310—320° (2 g.) and leaving a small tarry residue. Fraction (a) darkened in the air and solidified at 0°. Crystallisation from dilute alcohol yielded dimethyl-β-naphthylamine in white leaflets, m. p. 46° (cf. Hantzsch, *Ber.*, 1880, **13**, 2055; Pinnow, *loc. cit.*). Treatment with boiling methyl iodide gave β-naphthyltrimethylammonium iodide, which crystallised from alcohol in white leaflets, m. p. 190° (decomp.) (cf. Reychler, *Bull. Soc. chim.*, 1902, **27**, 886). The *picrate* crystallised from benzene in small yellow prisms, m. p. 195° (decomp.), almost insoluble in absolute alcohol; when crystallised from benzene–alcohol, it retained solvent of crystallisation (Found : N, 12·6, 12·9%), but it separated from acetone in small yellow prisms, m. p. 195—196° (decomp.) (Found: N, 14·1. $C_{10}H_7 \cdot NMe_2, C_6H_3O_7N_3$ requires N, 14·0%) (cf. Hodgson and Crook, this vol., p. 1502).

The benzene solution (W) was dried (sodium sulphate) and evaporated; the residual oil (20 g.) partly solidified. After filtration the solid residue was crystallised from benzene and yielded di-β-naphthylamine in lustrous white leaflets, m. p. 170° (cf. Ris, *Ber.*, 1887, **20**, 2618; Merz and Weith, *Ber.*, 1880, **13**, 1300; Heap, *loc. cit.*). The picrate separated from benzene in bronze needles, m. p. 164° (cf. Benz, *Ber.*, 1883, **16**, 20; Heap, *loc cit.*). Distillation of the oily filtrate gave two fractions, (a) b. p. 265—295° (4 g.) and (b) b. p. 295—355° (1 g.), and a viscous residue (5 g.). Fraction (b), treated with a hot alcoholic solution of picric acid, yielded a further quantity of di-β-naphthylamine picrate, m. p. and mixed m. p. 163—164°. Fraction (a) solidified on standing and crystallisation from light petroleum (b. p. 60—80°) yielded β-methoxynaphthalene in white flakes, m. p. and mixed m. p. 73—74° (Found : C, 83·5; H, 6·4. Calc. for $C_{11}H_{10}O$: C, 83·5; H 6·3%) (cf. Marchetti, *Gazzetta*, 1879, **9**, 545; Staedel, *Annalen*, 1883, **217**, 43).

(E) *With* 4 *mols. of methyl alcohol.* β-Naphthylamine hydrochloride (50 g.) and methyl alcohol (36 g.) were heated at 240—250° for 12 hours. The product was extracted from the autoclave with the aid of benzene, separated by decantation from a crystalline sediment, and shaken successively with aqueous alkali and acid, as described in experiment D. During the latter operation, as before, a yellow solid was precipitated. The crystalline sediment (13 g.) was washed with benzene. It was readily soluble in water and, when heated with aqueous sodium hydroxide, evolved a gas which had a fishy odour and burned with a non-luminous flame :

nitrogen was freely liberated on treatment with nitrous acid. These facts indicate that the substance is methylamine hydrochloride.

Acidification of the aqueous alkaline washings precipitated a solid (7 g.), which after two crystallisations from light petroleum (b. p. 60—80°) yielded 1-methyl-2-naphthol in long white needles, m. p. 110° (Found: C, 83·4; H, 6·5. Calc. for $C_{11}H_{10}O$: C, 83·5; H, 6·3%) (cf. Betti and Mundici, *Gazzetta*, 1906, **36**, 657; Fries and Hübner, *Ber.*, 1906, **39**, 441). Alkaline solutions of the naphthol exhibited a blue fluorescence and yielded no coloured precipitate on addition of a solution of benzenediazonium chloride (cf. Fries and Hübner, *loc. cit.*). The picrate separated from alcohol in red needles, m. p. 160—161° (cf. Betti and Mundici, *loc. cit.*; Bargellini and Silvestri, *Gazzetta*, 1907, **37**, 412; Dziewonski and Dragan, *loc. cit.*). Both the naphthol (m. p. 110°) and its picrate (m. p. 160—161°) showed marked depressions in m. p. when mixed with β-naphthol (m. p. 122°) and its picrate (m. p. 156°) respectively.

Addition of aqueous sodium hydroxide to the aqueous acid washings liberated strong fish-like odours, but only a small quantity of basic material was extracted with benzene. This distilled at 270—300°, became dark on standing, and yielded a picrate, m. p. 195—196° (decomp.) (from benzene–alcohol). No depression in m. p. was shown on admixture with dimethyl-β-naphthylamine picrate (see experiment D).

The residual benzene solution, containing neutral or weakly basic products, was dried over sodium sulphate and evaporated. The viscous oily residue (10 g.) was distilled and gave two fractions, (a) b. p. 260—340° (1·5 g.) and (b) b. p. above 340° (7·0 g.), both of which partly solidified. The solid from fraction (a), on recrystallisation, yielded β-methoxynaphthalene (m. p. and mixed m. p. 73—74°), and that from fraction (b), on crystallisation from benzene, gave mainly di-β-naphthylamine (m. p. and mixed m. p. 169—170°). Evaporation of the benzene mother-liquor left a yellow solid residue which, on repeated crystallisation from benzene–alcohol, yielded 3 : 4 : 6 : 7-dibenzacridine (m. p. 210°), a second compound in yellow needles, m. p. 183—184° (Found: C, 83·3; H, 4·9; N, 4·1%), and a yellow crystalline solid, m. p. 170—180°: the quantities of the last two compounds were insufficient for further examination.

The yellow hydrochloride which had separated when the benzene solution of the reaction product was shaken with hydrochloric acid was suspended in hot water and treated with aqueous sodium hydroxide. The liberated base (10 g.) was washed with water and dried. Fractional crystallisation from benzene–alcohol yielded mainly 3 : 4 : 6 : 7-dibenzacridine in fine yellow needles, m. p. 213—214° (Found: C, 90·2; H, 4·7; N, 5·3. Calc. for $C_{21}H_{13}N$: C, 90·3; H, 4·7; N, 5·0%) (cf. Reed, *J. pr. Chem.*, 1886, **34**, 160; 1887, **35**, 298; Morgan, J., 1898, **73**, 542; 1900, **77**, 814; Senier and Goodwin, J., 1902, **81**, 289; Senier and Austin, J., 1906, **89**, 1393; Kermack, Slater, and Spragg, *Proc. Roy. Soc. Edinburgh*, 1930, **50**, 243), and a small quantity of a second dibenzacridine in pale yellow needles, m. p. 206—207° (Found: C, 90·0; H, 5·0; N, 5·1%), regarded as 2 : 3 : 6 : 7-dibenzacridine (Strohbach, *Ber.*, 1901, **34**, 4157, gives m. p. 205·5—206° for this compound). The 3 : 4 : 6 : 7-dibenzacridine, which separated from alcohol in yellow needles or from benzene in brown leaflets, showed no depression in m. p. in admixture with an authentic specimen. Solutions in alcohol showed a strong blue-purple fluorescence, and in concentrated sulphuric acid solution a blue-green fluorescence was exhibited (cf. Senier and Goodwin, *loc. cit.*; Ullmann and Fetvadjian, *Ber.*, 1903, **36**, 1028). Solutions of 2 : 3 : 6 : 7-dibenzacridine in alcohol also showed a blue-purple fluorescence, and in concentrated sulphuric acid a yellow-green fluorescence.

The authors express their grateful thanks to Professor J. W. Cook for specimens of 1 : 2 : 6 : 7- and 3 : 4 : 6 : 7-dibenzacridine, to Dr. W. O. Kermack for a specimen of 1 : 2 : 8 : 9-dibenzacridine, and to the Chemical Society for a grant.

THE UNIVERSITY, MANCHESTER. [*Received, September 30th,* 1936.]