Pyrimidine Derivatives and Related Compounds. Part XXVI.[1] Oxidative and Non-oxidative Photocyclisations of 5-and 6-Phenylthio- and Anilino-1,3-dimethyluracils to Benzothienopyrimidines and Pyrimidoindoles

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Oxidative photocyclisation of the uracil derivatives (I) and (II), having an *N*-methylanilino-, a phenylthio-, or an anilino-group at the 5- or the 6-position, gives the corresponding benzothienopyrimidines (IIIa) and (IVa) and the pyrimidoindoles (IIIb and c) and (IVb). Under non-oxidative conditions, irradiation of 5-(*N*-methylanilino)- and 5-(*N*-acetylanilino)-1,3-dimethyluracil [(Ib) and (X)] gives the *trans*-dihydropyrimido[5,4-*b*]indoles (IX) and (XI) in high yields. The *trans* stereochemistry and the mechanism of formation of these dihydro-compounds are explained in terms of orbital symmetry arguments and deuterium labelling results.

PHOTOCYCLISATION (oxidative or non-oxidative) of *cis*-stilbenes,[2] diphenylamines,[3] *N*-aryl enamines,[4] and related systems[5] has been studied extensively and is regarded as a convenient route to condensed cyclic compounds. Photocyclisation of less aromatic heterocycles, however, has received less attention as a synthetic process, apart from a few examples.[6] We report here that oxidative photocyclisation of 5- and 6-phenylthio- and anilino-uracils [(I) and (II)] gives benzothienopyrimidines and pyrimidoindoles [(III) and (IV)], and photocyclisation of the 5-anilinouracil derivatives (Ib), (X), and (XIV) under non-oxidative conditions gives the *trans*-4a,9b-dihydropyrimidoindoles (IX), (XI), and (XV).

Irradiation of 5-phenylthio-, 5-(*N*-methylanilino)-,

[1] Part XXV, S. Senda, K. Hirota, and T. Asao, *J. Org. Chem.*, in the press.

[2] For reviews, see W. E. V. Blackburn and C. J. Timmons, *Quart. Rev.*, 1963, **85**, 2186; F. R. Stermitz, in 'Organic Photochemistry,' vol. 1, ed. O. L. Chapman, Marcel Dekker, New York, 1967, pp. 247—282; S. T. Reid, *Adv. Heterocyclic Chem.*, 1970, **6**, 87.

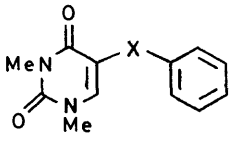
[3] C. A. Parker and W. J. Bernes, *Analyst*, 1957, **82**, 606; E. J. Bowen and J. H. D. Eland, *Proc. Chem. Soc.*, 1963, 202; W. Carruthers, *Chem. Comm.*, 1966, 272; V. M. Clark and E. J. Herbert, *J. Chem. Soc.* (*C*), 1968, 831.

[4] (*a*) O. L. Chapman, G. L. Eian, A. Bloom, and J. Clardy, *J. Amer. Chem. Soc.*, 1971, **93**, 2918; (*b*) K. Yamada, T. Konakahara, and H. Iida, *Bull. Chem. Soc. Japan*, 1973, **46**, 2504.

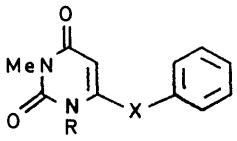
[5] E. Winterfeldt, *Angew. Chem.*, 1968, **80**, 486; Y. Kanaoka, *Synthesis*, 1972, 36; A. G. Schults and M. B. DeTar, *J. Amer. Chem. Soc.*, 1974, **96**, 296; I. Ninomiya, *Heterocycles*, 1974, **2**, 105.

[6] F. Yoneda and T. Nagamatsu, *Heterocycles*, 1974, **2**, 153.

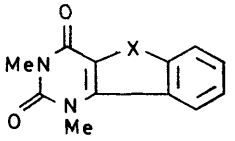
and 5-anilino-1,3-dimethyluracil (Ia—c) in acetone in the presence of air caused oxidative cyclisation giving the benzothieno[3,2-*d*]pyrimidine (IIIa) and pyrimido-[5,4-*b*]indoles (IIIb and c) in 9, 31, and 16% yields,



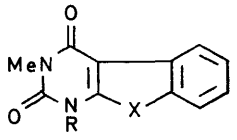
(I) a ; X = S
b ; X = NMe
c ; X = NH



(II) a ; R = Me X = S
b ; R = H X = NMe
c ; R = Me X = NH
d ; R = Me X = O



(III) a ; X = S
b ; X = NMe
c ; X = NH



(IV) a ; R = Me X = S
b ; R = H X = NMe

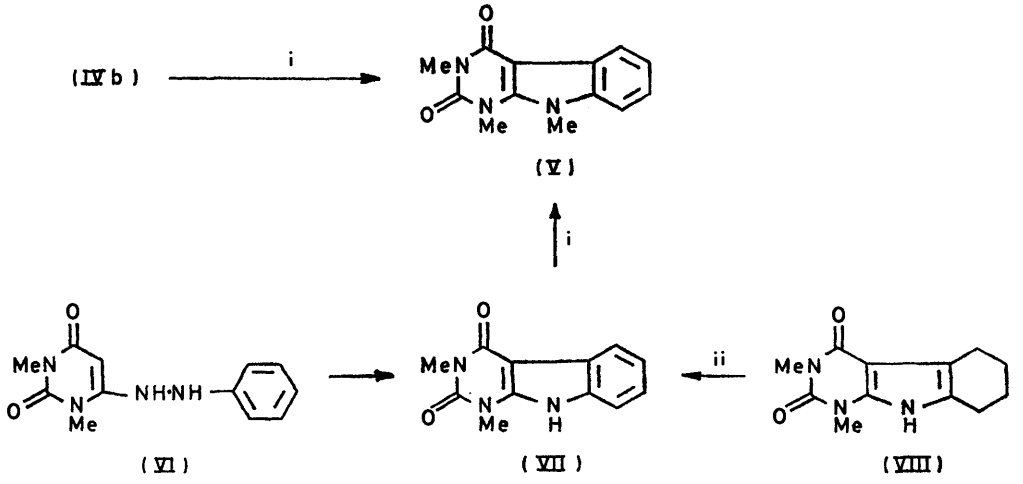
respectively. A similar intranuclear cyclisation occurred with the 6-phenylthio- and 6-(*N*-methylanilino)-uracil derivatives (IIa and b), affording the benzothieno[2,3-*d*]pyrimidine (IVa) [7] and the pyrimido-[4,5-*b*]indole (IVb), respectively. The latter was further methylated with dimethyl sulphate in aqueous 1% sodium hydroxide to give the 1,3,9-trimethylpyrimido-[4,5-*b*]indole (V), which was identical with an authentic sample prepared as follows. 1,3-Dimethyl-6-phenylhydrazinouracil (VI) [8] was subjected to the Fischer indole synthesis and the resulting 1,3-dimethylpyrimido-[4,5-*b*]indole (VII), which was also prepared by oxidation of 1,3-dimethyl-5,6,7,8-tetrahydro-1,3-dimethylpyrimido[4,5-*b*]indole-2,4(1*H*,3*H*)-dione (VIII) [9] with sulphur, was methylated with dimethyl sulphate to give the desired compound (V). No photocyclisation was observed with 6-anilino- and 6-phenoxy-1,3-dimethyluracils (IIc and d) under the same conditions.

In order to elucidate the mechanism of the oxidative cyclisation, the photoreaction of the 5-anilinouracils under non-oxidative conditions was examined. Irradiation of the 5-(*N*-methylanilino)uracil (Ib) in propan-2-ol under nitrogen gave the 4a,9b-dihydropyrimido[5,4-*b*]indole (IX) in 87% yield. The n.m.r. spectrum of the product showed double doublets at δ 3·81 and 4·75 (*J* 7·2 Hz), assignable to the 4a- and 9b-protons. Specific assignments to 4a- and 9b-protons were made on the basis of comparison with spectra of other dihydro-compounds [(XI), (XIII), and (XV)] prepared under the same conditions (see Table).

^{1}H N.m.r. data (solvent $CDCl_3$)

	Chemical shift (δ)	
Compound	4a-H	9b-H
(IX)	3·81	4·75
(XI)	5·02	5·23
(XIII)	3·81	
(XV)	3·53	

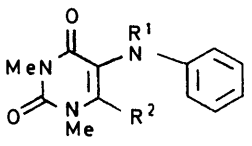
The configuration at positions 4a and 9b could not be assigned rigorously, but it is believed that the 4a- and 9b-protons are *trans*, as demonstrated for the principal products of many other non-oxidative photocyclisations. Orbital symmetry arguments [10] suggest that cyclisation of (Ib) in a photoexcited state should occur in a conrotatory manner. Demotion of the excited state (XVI) should then lead to a dipolar ion



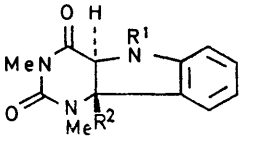
SCHEME 1 Reagents: i, Me_2SO_4–aq. NaOH; ii, S

[7] R. D. Youssefyeh and M. Weise, *Tetrahedron Letters*, 1973, 4317.
[8] S. Senda, K. Hirota, and G.-N. Yang, *Chem. and Pharm. Bull.* (*Japan*), 1972, **20**, 399.
[9] S. Senda and K. Hirota, *Chem. and Pharm. Bull.* (*Japan*), 1974, **22**, 1459.
[10] R. B. Woodward and R. Hoffman, *Angew. Chem. Internat. Edn.*, 1959, **8**, 781, and references cited therein.

intermediate (XVII) analogous to the one observed in the oxidative photocyclisation of diphenylamine.[11] A hydrogen migration occurring in the intermediate (XVII) to give the product (IX) must be a suprafacial shift. Both a [1,4] hydrogen shift and two consecutive [1,2] shifts in the ground state (XVII) are allowed and have been considered previously.[4a,12]



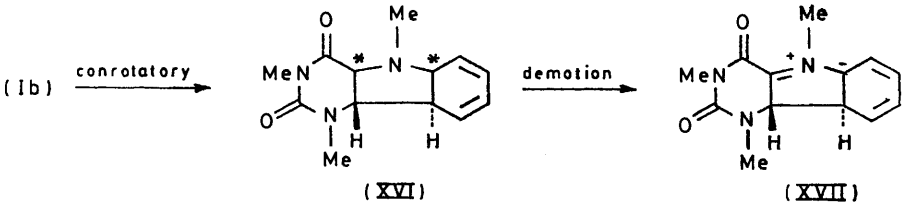
(X) R^1 = Ac, R^2 = H
(XII) R^1 = Me, R^2 = D
(XIV) R^1 = Me, R^2 = Me



(IX) R^1 = Me, R^2 = H
(XI) R^1 = Ac, R^2 = H
(XIII) R^1 = Me, R^2 = D
(XV) R = Me, R = Me

In order to determine the pattern of the hydrogen shift, the non-oxidative photocyclisation of 6-deuterio-1,3-dimethyl-5-(*N*-methylanilino)uracil (XII), prepared from 5-bromo-6-deuteriouracil[13] in two steps, was investigated, and the 9b-deuterio-4a,9b-*trans*-compound (XIII) was obtained. Similarly, 5-(*N*-methylanilino)-1,3,6-trmethyluracil (XIV) gave the 9b-methyl compound (XV). These results indicate that only a [1,4] hydrogen shift is important in the transformation of (XVII) into (IX).

Irradiation of the dihydro-compound (IX) in propan-2-ol in the precence of air afforded the dehydrogenated product (IIIb) in 32% yield. The foregoing experimental results suggest that a path for the oxidative photocyclisation of (Ib) to (IIIb) involves the dihydro-compound (IX) and proceeds *via* the dipolar ion intermediate (XVII), although an alternative path involving direct dehydrogenation of the intermediate (XVII) is not ruled out.



SCHEME 2

EXPERIMENTAL

M.p.s were determined with a Yanagimoto micro apparatus. ^{1}H N.m.r. spectra were measured with a Hitachi–Perkin-Elmer R-20B spectrometer, with tetramethylsilane as internal reference.

Irradiation of Uracils.—Preparative irradiations were carried out in a flask equipped with a Pyrex-jacketed immersion lamp. The light source was a Riko-UVL 100 W high-pressure mercury lamp. Oxidative reactions were carried out in acetone or propan-2-ol in the presence of air. For non-oxidative reactions, freshly distilled propan-2-ol was used as solvent, the solution was stirred, and nitrogen was bubbled through throughout the irradiation.

1,3-*Dimethyl*-5-*phenylthiouracil* (Ia).—To a solution of sodium ethoxide [from sodium (0·46 g, 0·02 mol)] and benzenethiol (2·2 g, 0·020 mol) in absolute ethanol (50 ml) was added 5-bromo-1,3-dimethyluracil (4·4 g, 0·02 mol). The mixture was refluxed for 1 h. Evaporation left a white solid, which was washed with water to give *compound* (Ia) (2·9 g, 61%), m.p. 136° (from benzene) (Found: C, 58·0; H, 4·7; N, 11·15. $C_{12}H_{12}N_2O_2S$ requires C, 58·05; H, 4·85; N, 11·3%), δ ($CDCl_3$) 3·37 (3H, s, NMe), 3·40 (3H, s, NMe), 7·1—7·4 (5H, m, aromatic), and 7·69 (1H, s, 6-H).

1,3-*Dimethyl*-5-(N-*methylanilino*)*uracil* (Ib).—Dimethyl sulphate (4·7 g, 0·037 mol) was added dropwise during 1 h to a stirred solution of 5-(*N*-methylanilino)uracil[14] (3·5 g, 0·016 mol) in aqueous 10% sodium hydroxide (15 ml). The precipitate was filtered off to give the methylated *product* (Ib) (2·7 g, 58%), m.p. 145° (from benzene) (Found: C, 63·4; H, 6·15; N, 16·85. $C_{13}H_{15}N_3O_2$ requires C, 63·65; H, 6·15; N, 17·15%), δ ($CDCl_3$) 3·18 (3H, s, NMe) 3·42 (3H, s, NMe), 6·6—7·5 (5H, m, aromatic), and 7·32 (1H, s, 6-H).

5-*Anilino*-1,3-*dimethyluracil* (Ic).—5-Anilinouracil[14] was treated as described in the preparation of (Ib) to give the 1,3-*dimethyl compound* (Ic) (59%), m.p. 138° (from benzene) (Found: C, 62·05; H, 5·65; N, 18·05. $C_{12}H_{13}N_3O_2$ requires C, 62·3; H, 5·65; N, 18·15%), δ ($CDCl_3$) 3·40 (3H, s, NMe), 3·44 (3H, s, NMe), 5·3—6·2br (1H, NH), and 6·75—7·50 (6H, m, aromatic and 6-H).

1,3-*Dimethyl*-6-*phenylthiouracil* (IIa).—6-Chloro-1,3-dimethyluracil[15] was treated as described in the preparation of (Ia) to give the 6-*phenylthiouracil* (IIa) (75%), m.p. 137° (from benzene) (Found: C, 58·25; H, 4·9; N, 11·3. $C_{12}H_{12}N_2O_2S$ requires C, 58·05; H, 4·85; N, 11·3%), δ ($CDCl_3$) 3·32 (3H, s, NMe), 3·59 (3H, s, NMe), 5·06 (1H, s, 5-H), and 7·57 (5H, s, aromatic).

1,3-*Dimethyl*-6-*phenoxyuracil* (IId).—A solution of sodium ethoxide [from sodium (0·4 g, 0·017 mol)] and phenol (2·0 g, 0·023 mol) in absolute ethanol (50 ml) was refluxed for 30 min. 6-Chloro-1,3-dimethyluracil (3·9 g, 0·017 mol) was added, and then the mixture was refluxed for 1 h. The solvent was evaporated off and the resulting solid was washed with water to give the 6-*phenoxyuracil* (IId) (2·9 g,

[11] K.-H. Grellmann, G. M. Sherman, and H. Linschitz, *J. Amer. Chem. Soc.*, 1963, **85**, 1881; H. Linschitz and K.-H. Grellmann, *ibid.*, 1964, **86**, 303.
[12] M. T. Rwetz, *Tetrahedron*, 1973, **29**, 2189.
[13] C. Parkanyi and F. Sorm, *Coll. Czech. Chem. Comm.*, 1963, **28**, 2941.
[14] F. R. Gerns, A. Perrotaa, and G. H. Hitching, *J. Medicin. Chem.*, 1966, **9**, 108.
[15] W. Pfleiderer and K. H. Schündehütte, *Annalen*, 1958, **612**, 158.

73%), m.p. 120° (from ether) (Found: C, 62·15; H, 5·2; N, 12·15. $C_{12}H_{12}N_2O_3$ requires C, 62·05; H, 5·2; N, 12·05%), δ ($CDCl_3$) 3·35 (3H, s, NMe), 3·57 (3H, s, NMe), 4·82 (1H, s, 5-H), and 7·05—7·65 (5H, m, aromatic).

1,3-*Dimethyl*[1]*benzothieno*[3,2-d]*pyrimidine*-2,4(1H,3H)-*dione* (IIIa).—A solution of the uracil (Ia) (0·60 g, 0·0024 mol) in acetone (200 ml) was irradiated for 24 h. The solvent was evaporated off and the residue washed with acetone to give the *benzothienopyrimidine* (IIIa) (50 mg, 9%), m.p. 251° (from ethyl acetate) (Found: C, 58·3; H, 4·15; N, 11·35. $C_{12}H_{10}N_2O_2S$ requires C, 58·55; H, 4·1; N, 11·4%), δ ($CDCl_3$) 3·54 (3H, s, NMe) 4·10 (3H, s, NMe), and 7·3—8·5 (4H, m, aromatic).

1,3,5-*Trimethylpyrimido*[5,4-b]*indole*-2,4(1H,3H)-*dione* (IIIb).—(*a*) After irradiation of a solution of the uracil (Ib) (0·90 g, 0·0037 mol) in acetone (200 ml) for 2 h, the precipitate was filtered off to give the *5-methylpyrimidoindole* (IIIb) (280 mg, 31%), m.p. >300° (Found: C, 64·2; H, 5·4; N, 17·35. $C_{13}H_{13}N_3O_2$ requires C, 64·2; H, 5·4; N, 17·3%).

(*b*) *Photodehydrogenation of compound* (IX). A solution of compound (IX) (400 mg, 0·0016 mol) in propan-2-ol (300 ml) was irradiated in the presence of air for 17 h. The precipitate afforded the dehydrogenated product (IIIb) (125 mg, 32%), identical with the sample obtained in (*a*).

1,3-*Dimethylpyrimido*[5,4-b]*indole*-2,4(1H,3H)-*dione* (IIIc).—A solution of the uracil (Ic) (800 mg, 0·0034 mol) in acetone (200 ml) was irradiated for 24 h. Filtration gave the *pyrimidoindole* (IIIc) (130 mg, 16%), m.p. >300° (from acetic acid) (Found: C, 62·8; H, 4·85; N, 18·35. $C_{12}H_{11}N_3O_2$ requires C, 62·85; H, 4·85; N, 18·35%).

1,3-*Dimethyl*[1]*benzothieno*[2,3-d]*pyrimidine*-2,4(1H,3H)-*dione* (IVa).—After irradiation of a solution of the uracil (IIa) (800 mg, 0·0032 mol) in acetone (200 ml) for 24 h, the solvent was evaporated off. The oily residue was treated with acetone and the solid filtered off to give the *benzothienopyrimidine* (IVa) (235 mg, 30%), m.p. 194° (from ethyl acetate) (Found: C, 58·45; H, 4·15; N, 11·35. $C_{12}H_{10}N_2O_2S$ requires C, 58·55; H, 4·1; N, 11·4%), δ ($CDCl_3$) 3·47 (3H, s, NMe), 3·57 (3H, s, NMe), and 7·2—7·9 and 8·5 (4H, m, aromatic).

3,9-*Dimethylpyrimido*[4,5-b]*indole*-2,4(1H,3H)-*dione* (IVb).—A solution of 3-methyl-6-(*N*-methylanilino)uracil [16] (900 mg, 0·0037 mol) in acetone (200 ml) was irradiated for 24 h. Filtration gave the *pyrimidoindole* (IVb) (273 mg, 31%), m.p. >300° (from ethanol) (Found: C, 62·7; H, 4·75; N, 18·05. $C_{12}H_{11}N_3O_2$ requires C, 62·85; H, 4·85; N, 18·35%).

1,3,9-*Trimethylpyrimido*[4,5-b]*indole*-2,4(1H,3H)-*dione* (V).—(*a*) To a stirred solution of the pyrimidoindole (IVb) (250 mg, 0·0011 mol) in aqueous 1% sodium hydroxide was added dimethyl sulphate (280 mg, 0·0022 mol). The precipitate was filtered off to give the 1,3,9-*trimethylpyrimidoindole* (V) (241 mg, 91%), m.p. 248° (from methanol) (Found: C, 64·3; H, 5·55; N, 17·5. $C_{13}H_{13}N_3O_2$ requires C, 64·2; H, 5·4; N, 17·3%).

(*b*) Dimethyl sulphate (1·4 g, 0·011 mol) was added to a stirred solution of the pyrimidoindole (VII) (2·3 g, 0·01 mol) in aqueous 5% sodium hydroxide (10 ml). The precipitate afforded the trimethylpyrimidoindole (V) (2·0 g, 83%), identical with the sample prepared in (*a*).

1,3-*Dimethylpyrimido*[4,5-b]*indole*-2,4(1H,3H)-*dione* (VII).—(*a*) A solution of 1,3-dimethyl-6-phenylhydrazinouracil (VI) [8] (2·4 g, 0·01 mol) in tetralin (30 ml) was refluxed for 30 min. After cooling, the precipitate was collected to give the *cyclisation product* (VII) (2·0 g, 89·5%), m.p. >300° (from dimethylformamide–ethanol) (Found: C, 62·95; H, 5·0; N, 18·05. $C_{12}H_{11}N_3O_2$ requires C, 62·85; H, 4·85; N, 18·35%).

(*b*) A mixture of 5,6,7,8-tetrahydro-1,3-dimethylpyrimido[4,5-b]indole-2,4(1*H*,3*H*)-dione (VIII) [9] (2·3 g, 0·01 mol), sulphur (1 g), and quinoline (25 ml) was refluxed for 30 min, cooled, and poured into dilute hydrochloric acid. The precipitate was filtered off to give the oxidized product (VIII) (0·7 g, 30%), identical with the sample prepared in method (*a*).

trans-4a,9b-*Dihydro*-1,3,5-*trimethylpyrimido*[5,4-b]*indole*-2,4(1H,3H)-*dione* (IX).—A solution of the uracil (Ib) (1·60 g, 0·0065 mol) in propan-2-ol (800 ml) was irradiated under nitrogen for 4 h. The solvent was evaporated off and the residue was washed with ether to give the trans-4a,9b-*dihydropyrimidoindole* (IX) (1·31 g, 87%), m.p. 128° (from petroleum) (Found: C, 63·5; H, 6·2; N, 17·05. $C_{13}H_{15}N_3O_2$ requires C, 63·65; H, 6·15; N, 17·15%), δ ($CDCl_3$) 2·93, 3·02, and 3·27 (each 3H, s, NMe), 3·81 and 4·75 (2H, double doublets, *J* 7·5 Hz, 4a- and 9b-H), and 6·60—7·5 (4H, m, aromatic), *m/e* 245 (M^+).

5-(N-*Acetylanilino*)-1,3-*dimethyluracil* (X).—A solution of the uracil (Ic) (1·0 g, 0·0045 mol) and acetyl chloride (1·5 g, 0·02 mol) in chloroform (10 ml) was refluxed for 1 h, then evaporated. The residue was dissolved in water (30 ml). The solution was extracted with chloroform and the extract was dried and evaporated. Column chromatography of the product (silica gel; chloroform) gave 5-(N-*acetylanilino*)-1,3-*dimethyluracil* (0·85 g, 71%), m.p. 127° (Found: C, 61·3; H, 5·55; N, 15·5. $C_{14}H_{15}N_3O_3$ requires C, 61·55; H, 5·55; N, 15·4%), δ ($CDCl_3$) 2·08 (3H, s, Ac), 3·42 (6H, s, 2NMe), and 7·47 (6H, s, 6-H and aromatic).

trans-5-*Acetyl*-4a,9b-*dihydro*-1,3-*dimethylpyrimido*-[5,4-b]-*indole*-2,4(1H,3H)-*dione* (XI).—After irradiation of a solution of the uracil (X) (450 mg, 0·0016 mol) in propan-2-ol (300 ml) under nitrogen for 3 h, the solvent was evaporated off and the residue was washed with ether to give the trans-4a,9b-*dihydro-compound* (XI) (410 mg, 91%), m.p. 226° (from ethyl acetate) (Found: C, 61·65; H, 5·5; N, 15·35. $C_{14}H_{15}N_3O_2$ requires C, 61·55; H, 5·55; N, 15·4%), δ ($CDCl_3$) 2·44 (3H, s, Ac), 3·16 (3H, s, NMe), 3·46 (3H, s, NMe), and 5·02 and 5·23 (2H, double doublets, *J* 7·5 Hz, 4a- and 9b-H).

6-*Deuterio*-1,3-*dimethyl*-5-(N-*methylanilino*)*uracil* (XII).—A mixture of 5-bromo-6-deuteriouracil [13] (1·7 g, 0·0089 mol) and *N*-methylaniline (4·8 g, 0·045 mol) in ethylene glycol (10 ml) was refluxed for 3 h. After cooling, water (20 ml) was added. The precipitate was filtered off to give 6-deuterio-5-(*N*-methylanilino)uracil (0·8 g, 41%). Without purification, the product was treated as described in the preparation of (Ib) to give 6-*deuterio*-1,3-*dimethyl*-5-(N-*methylanilino*)*uracil* (60%), m.p. 144° (from benzene), *m/e* 246 (M^+). The amount of deuterium at the 6-position was shown to be 90% by mass spectral analysis.

trans-9b-*Deuterio*-4a,9b-*dihydro*-1,3,5-*trimethylpyrimido*-[5,4-b]*indole*-2,4(1H,3H)-*dione* (XIII).—A solution of compound (XII) (144 mg, 0·00059 mol) in propan-2-ol (250 ml) was treated as in the preparation of (IX) to give the 9b-*deuterio-compound* (XIII) (125 mg, 86%), m.p. 127° (from petroleum). The ^1H n.m.r. spectrum ($CDCl_3$)

[16] F. Yoneda, Y. Sakuma, M. Ichiba, and K. Shinomura, *Chem. and Pharm. Bull.* (*Japan*), 1972, **20**, 1832.

showed that the deuterium content at position 9b was 90%.

1,3,6-*Trimethyl*-5-(N-*methylanilino*)*uracil* (XIV).—A mixture of 5-anilino-6-methyluracil [15] (1·41 g, 0·0062 mol), methyl iodide (13·8 g, 0·09 mol), and anhydrous potassium carbonate (2·6 g, 0·0062 mol) in dimethylformamide (15 ml) was refluxed with stirring for 8 h. The solvent was evaporated off and the residue washed with water to give the *permethylated compound* (XIV) (1·3 g, 81%), m.p. 157° (from n-hexane) (Found: C, 64·95; H, 6·65; N, 16·2. $C_{14}H_{15}N_3O_2$ requires C, 64·85; H, 6·6; N, 16·2%), δ ($CDCl_3$) 2·23 (3H, s, 6-Me), 3·15, 3·37, and 3·45 (each 3H, s, NMe), and 6·5—7·4 (5H, m, aromatic).

4a,9b-*Dihydro*-1,3,5,9b-*tetramethylpyrimido*[5,4-b]*indole*-2,4(1H,3H)-*dione* (XV).—After irradiation of a solution of compound (XIV) (500 mg, 0·0019 mol) in propan-2-ol (300 ml) under nitrogen for 4 h, the solvent was evaporated off and the residue was triturated with ether. The solid was filtered off to give the 9b-*methyl compound* (XV) (280 mg, 56%), m.p. 222° (from ethyl acetate) (Found: C, 64·65; H, 6·6; N, 16·35. $C_{14}H_{15}N_3O_2$ requires C, 64·85; H, 6·6; N, 16·2%), δ ($CDCl_3$) 1·63 (3H, s, 9b-Me), 2·82 (3H, s, NMe), 3·53 (1H, s, 4a-H), 3·85 (3H, s, NMe), and 6·6—7·5 (4H, m, aromatic).

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