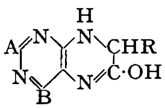
126. *Pteridines. Part II. The Synthesis of Some α-(5-Nitro-4-pyrimidylamino)-ketones and Their Conversion into 7 : 8-Dihydropteridines and Pteridines.*

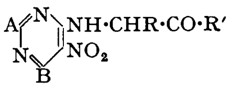
By W. R. Boon and W. G. M. Jones.

Condensation of 4-chloro-5-nitropyrimidines with α-amino-ketones gives α-(5-nitro-4-pyrimidylamino)-ketones, reduction of which provides an unambiguous and useful synthesis of 7 : 8-dihydropteridines and pteridines.

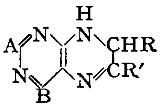
In Part I (*J.*, 1951, 96) a method for the preparation of 6-hydroxy-7 : 8-dihydropteridines (I) of unambiguous structure was described, involving the reduction and subsequent cyclisation of α-(5-nitro-4-pyrimidylamino)-esters (II; R′ = OMe or OEt). We now describe similar reactions for α-(5-nitro-4-pyrimidylamino)-ketones (II; R = H or a hydrocarbon radical, R′ = a hydrocarbon radical), which are particularly useful for the preparation of 7 : 8-dihydropteridines of type (III) (cf. Boon, Jones, and Imperial Chemical Industries Ltd., B.P. 635,582). Recently Polonovski, Pesson, and Puister (*Compt. rend.*, 1950, **230**, 2205) have prepared 2-ethoxy-7 : 8-dihydro-4-methyl-6 : 7-diphenylpteridine by a similar route.



(I.)



(II.)



(III.)

Owing to the generally greater tendency of α-amino-ketones than of α-amino-esters to undergo self-condensation, it was not possible to cause the chloronitropyrimidine to react with the free amino-ketone. Good results were obtained, however, by allowing a suspension of the amino-ketone hydrochloride to react with a solution of the chloronitropyrimidine in an inert solvent in the presence of a mild alkali, such as sodium hydrogen carbonate. Thus, 2 : 4-dichloro-5-nitropyrimidine was readily converted into 2-chloro-5-nitro-4-pyrimidylaminoacetone (II; A = Cl, B = R = H, R′ = Me) in 50% yield. Replacement of the second chlorine atom by an amino-, benzylamino-, or diethylamino-group proceeded smoothly, the resulting products being readily hydrogenated over Raney nickel to the corresponding dihydropteridines. Reduction of 2-chloro-5-nitro-4-pyrimidylaminoacetone did not proceed as smoothly as that of the corresponding ethyl 2-chloro-5-nitro-4-pyrimidylaminoacetate (Boon *et al.*, *loc. cit.*) : reduction in methanol solution over Raney nickel, at the ordinary temperature, ceased after the absorption of two moles of hydrogen, with the separation of an unstable product analysis of which approximated to that for 4-acetonylamino-2-chloro-5-pyrimidylhydroxylamine. This substance, which was soluble in both acid and alkali, reduced Fehling's solution and was decomposed when warmed. A solution in dimethylformamide absorbed a further mole of hydrogen over Raney nickel but no characterisable product could be isolated. Similarly, no crystalline product could be isolated after similar reduction of 2-chloro-6-methyl-5-nitro-4-pyrimidylaminoacetone.

Condensation of amino-ketones with 4 : 6-dichloro-5-nitropyrimidines was, in general, less satisfactory than that with the 2 : 4-dichloro-5-nitro-compounds, owing, in part, to the smaller difference in reactivity between the two chlorine atoms in the former case and, in part also, to the marked sensitivity of the 6-chloro-5-nitro-4-pyrimidylamino-ketones to moisture. In only one case has a product containing two α-amino-ketone residues been isolated : condensation of 4 : 6-dichloro-5-nitropyrimidine with α-aminodeoxybenzoin yields a mixture of α-(6-chloro-5-nitro-4-pyrimidylamino)benzyl phenyl ketone (II; A = H, B = Cl, R = R′ = Ph) and 5-nitro-4 : 6-di-(α-phenylphenacylamino)pyrimidine (II; A = H, B = NH·CHPh·CO·Ph, R = R′ = Ph). 6-Chloro-5-nitro-4-pyrimidylaminoacetone and the corresponding 2-methyl compound are readily hydrolysed by water to the corresponding 6-hydroxy-compounds, conversion being complete after a short exposure to moist air (which vitiates analysis). By working rapidly, however, it was possible to replace the second halogen atom smoothly by amino- or substituted amino-groups.

4-Chloro-6-ethoxy-2-methyl-5-nitropyrimidine did not react with aminoacetone under the usual conditions, but condensation with glycine methyl ester gave methyl 6-ethoxy-2-methyl-5-nitro-4-pyrimidylaminoacetate.

Oxidation of the dihydropteridines with alkaline permanganate proceeded readily in all cases so far examined. Thus, 4-amino-7 : 8-dihydro-6 : 7-dimethyl-, 4-amino-7 : 8-dihydro-6 : 7-diphenyl-, and 4-diethylamino-7 : 8-dihydro-6 : 7-diphenyl-pteridines gave pteridines identical with those obtained directly by condensation of the appropriate 4 : 5-diaminopyrimidine and α-diketone. In some cases, the required product was more readily obtained by oxidation of the dihydro-compound : *e.g.*, 4 : 5 : 6-triaminopyrimidine and benzil gave only a small yield of pteridine; 2 : 4 : 5-triaminopyrimidine and benzil gave none of the pteridine; and 4 : 5-diamino-2-diethylaminopyrimidine is sensitive to aerial oxidation.

4-Amino-6-diethylamino-5-nitropyrimidine was reduced smoothly over Raney nickel to 4 : 5-diamino-6-diethylaminopyrimidine. In addition to condensation with benzil, noted above, this substance reacted readily with glyoxal, diacetyl, acenaphthenequinone, phenanthraquinone, and furil to give the corresponding pteridines. Condensation with 4 : 4′-dichlorobenzil gave only a low yield of pteridine, and none was obtained from anisil.

EXPERIMENTAL.

Microanalyses are by Drs. Weiler and Strauss.

4-Amino-2-diethylamino-5-nitropyrimidine.—Diethylamine (9 g., 0·13 mol.) was added with cooling to a solution of 4-amino-2-chloro-5-nitropyrimidine (8·75 g., 0·05 mol.) in dioxan (100 c.c.). After 18 hours the diethylamine hydrochloride was filtered off and washed with dioxan. Evaporation of the filtrate to dryness and crystallisation of the residue from aqueous methanol gave *4-amino-2-diethylamino-5-nitropyrimidine* (9·9 g., 87%), m. p. 109—110° (Found : C, 45·9; H, 6·1; N, 33·3. $C_8H_{13}O_3N_5$ requires C, 45·5; H, 6·2; N, 33·2%).

4-Amino-6-diethylamino-5-nitropyrimidine, m. p. 119° (from aqueous methanol) (Found : C, 45·2; H, 6·2; N, 33·4. $C_8H_{13}O_2N_5$ requires C, 45·5; H, 6·2; N, 33·2%), and *4-amino-5-nitro-6-morpholinopyrimidine*, m. p. 182° (from benzene) (Found : C, 42·7; H, 4·9; N, 31·2. $C_8H_{11}O_3N_5$ requires C, 42·7; H, 4·9; N, 31·1%), were obtained similarly in 90% and 75% yield respectively from 4-amino-6-chloro-5-nitropyrimidine.

4-*Chloro*-6-*ethoxy*-2-*methyl*-5-*nitropyrimidine*.—To a cold solution of 4 : 6-dichloro-2-methyl-5-nitropyrimidine (10 g.) in absolute ethanol there was added, with stirring, a solution of sodium ethoxide (from 1·1 g. of sodium). After 1 hour the solution was poured into water, and the solid collected, dried on a tile and crystallised from light petroleum (b. p. 60—80°), giving 4-chloro-6-ethoxy-2-methyl-5-nitropyrimidine (9 g.), m. p. 81° (Found : C, 38·5; H, 3·5; N, 19·3. $C_7H_8O_3N_3Cl$ requires C, 38·6; H, 3·7; N, 19·2%). Similarly there were obtained 4-*chloro*-6-*ethoxy*-5-*nitropyrimidine*, b. p. 134—136°/16 mm., m. p. 42° [from light petroleum (b. p. 40—60°)] (Found : C, 35·6; H, 2·9; N, 20·2. $C_6H_6O_3N_3Cl$ requires C, 35·3; H, 3·0; N, 20·6%), from 4 : 6-dichloro-5-nitropyrimidine and sodium ethoxide (1 mol.) and 4 : 6-*diethoxy*-2-*methyl*-5-*nitropyrimidine*, m. p. 74° (from aqueous ethanol) (Found : C, 48·0; H, 6·1; N, 18·1. $C_9H_{13}O_4N_3$ requires C, 47·6; H, 5·7; N, 18·5%), from 4 : 6-dichloro-2-methyl-5-nitropyrimidine and sodium ethoxide (2 mols.).

Methyl 6-*Ethoxy*-2-*methyl*-5-*nitro*-4-*pyrimidylaminoacetate*.—Glycine methyl ester (4·2 g.) was added to a cold solution of 4-chloro-6-ethoxy-2-methyl-5-nitropyrimidine (5 g.) in methanol (30 c.c.). After 1 hour, the mixture was poured into water, and the solid collected and crystallised from aqueous methanol, giving *methyl* 6-*ethoxy*-2-*methyl*-5-*nitro*-4-*pyrimidylaminoacetate* (4 g.), m. p. 81° (Found : C, 44·5; H, 5·2; N, 20·2. $C_{10}H_{14}O_5N_4$ requires C, 44·4; H, 5·2; N, 20·7%).

2(6)-*Chloro*-5-*nitro*-4-*pyrimidylamino-ketones* (*Method* I).—The preparation of 2-*chloro*-5-*nitro*-4-*pyrimidylaminoacetone* is typical. To a stirred solution of 2 : 4-dichloro-5-nitropyrimidine (5 g., 0·026 mol.) in dry acetone (50 c.c.), sodium hydrogen carbonate (6 g.) was added, followed by aminoacetone hydrochloride (3·5 g., 0·032 mol.) during 2 hours. The reaction mixture was then filtered, the filtrate concentrated to dryness under reduced pressure, and the residue crystallised from light petroleum (b. p. 60—80°) containing a little ethyl acetate, giving 2-chloro-5-nitro-4-pyrimidylaminoacetone.

For reactions with a 4 : 6-dichloro-5-nitropyrimidine it was advantageous to have some anhydrous magnesium sulphate present during the condensation. In the case of α-(6-*chloro*-5-*nitro*-4-*pyrimidylamino*)*deoxybenzoin* the residue left after removal of the acetone was a glass consisting predominantly of a mixture of the desired product and 5-*nitro*-4 : 6-*di*-(α-*phenylphenacylamino*)*pyrimidine* which were separated by fractional crystallisation from light petroleum. For these and other products see Table I.

2(6)-*Amino*(*or Substituted Amino*)-5-*nitro*-4-*pyrimidylamino-ketones* (Method II).—The preparation of α-(6-*diethylamino*-5-*nitro*-4-*pyrimidylamino*)*deoxybenzoin* is typical. Diethylamine (7 g.), added to a solution of α-(6-chloro-5-nitro-4-pyrimidylamino)deoxybenzoin (16 g.) in ethyl acetate, produced an immediate yellow precipitate. After 4 hours the reaction mixture was evaporated to dryness and lixiviated with water to remove diethylamine hydrochloride. Crystallisation of the residue (1·65 g.) gave the desired product (1·5 g.). For this and other products see Table I.

7 : 8-*Dihydropteridines* (*Method* III).—The preparation of 4-*diethylamino*-7 : 8-*dihydro*-6 : 7-*diphenylpteridine* is typical. α-(6-Diethylamino-5-nitro-4-pyrimidylamino)deoxybenzoin (2·0 g.) in methanol (25 c.c.) was hydrogenated at room temperature and pressure over Raney nickel. After filtration the solution was evaporated to dryness and the residue crystallised, giving the dihydro-compound (1·2 g.). For this and other products see Table II.

4-*Diethylamino*-7 : 8-*dihydro*-6-*methylpteridine*.—To 6-chloro-5-nitro-4-pyrimidylaminoacetone (2·25 g.) in ethyl acetate (25 c.c.), diethylamine (1·8 g.) was added with cooling. After 14 hours the diethylamine hydrochloride was removed and the filtrate evaporated under reduced pressure. The residual oil (2·6 g.) was reduced in methanol (30 c.c.) with hydrogen over Raney nickel at room temperature and pressure. After removal of the catalyst and solvent the residue was crystallised (see Table II).

4-*Diethylamino*-7 : 8-*dihydro*-6 : 7-*dimethylpteridine*.—To a stirred solution of 4 : 6-dichloro-5-nitropyrimidine (6·0 g.) in dry acetone (60 c.c.) sodium hydrogen carbonate (7·7 g.) and anhydrous sodium sulphate (6·2 g.) were added, followed, during 35 minutes, by 3-aminobutan-2-one hydrochloride (3·8 g.). After 3 hours' stirring, the inorganic salts were filtered off and the solvent evaporated under reduced pressure. The residual oil was dissolved in cold ethyl acetate and filtered and the ethyl acetate removed under reduced pressure, giving an oil (8·1 g.) which could not be induced to crystallise. This was redissolved in ethyl acetate (50 c.c.), and diethylamine (7 g.) added to the solution with cooling. After being kept overnight the diethylamine hydrochloride was filtered off and the filtrate concentrated under reduced pressure to give an oil (8·4 g.), which could not be induced to crystallise either directly or after chromatography on an alumina column. The oil (6·8 g.) was reduced in methanol (100 c.c.) at 40 lbs./sq. in. hydrogen pressure over Raney nickel. After removal of the catalyst and solvent the residue, crystallised from light petroleum (b. p. 60—80°), gave crystals (2·35 g.), m. p. 85—105°. Recrystallisation from *n*-hexane gave material (1·8 g.) of m. p. 96—99°. This was then dissolved in water (90 c.c.), and sufficient hydrochloric acid added to make the solution just acid to Congo-red. The solution was then stirred with charcoal and filtered, the filtrate basified with aqueous ammonia, and the solid collected, washed with water, dried (m. p. 106—108°), and crystallised from much water (see Table II).

Pteridines (*Method* IV).—The preparation of 4-*diethylamino*-6 : 7-*diphenylpteridine* is typical.

(*a*) *By oxidation of the dihydropteridine.* To a solution of 4-diethylamino-7 : 8-dihydro-6 : 7-diphenylpteridine (0·4 g.) in acetone (25 c.c.) was added slowly, with stirring, a solution of potassium permanganate (0·12 g.) in acetone (75 c.c.). After being kept overnight and filtered, the solution was evaporated to dryness, and the residue dissolved in benzene and passed through activated alumina (15 g.). Development of the column with benzene gave an upper (unchanged material; 0·1 g.) and a lower zone which yielded 4-diethylamino-6 : 7-diphenylpteridine (0·2 g.), m. p. 156° alone or mixed with a sample prepared by method (*b*).

TABLE I.

α-(5-*Nitro-4-pyrimidylamino*)-*ketones* (II).

				Method of		Yield,			Found, %.				Required, %.			
A.	B.	R.	R′.	prepn.*	M. p.	%.	Solvent.†	Formula.	C.	H.	N.	Cl.	C.	H.	N.	Cl.
H	Cl	H	Me	I	60—61°	—	Pet., 2	$C_7H_7O_3N_4Cl$	Not analysed owing to rapid decomp. in air.							
Me	Cl	H	Me	I	84	—	Et_2O	$C_8H_9O_3N_4Cl$		,,	,,	,,		,,	,,	
Cl	H	H	Me	I	131	75	Pet., 1	$C_7H_7O_3N_4Cl$	36·6	3·0	24·6	—	36·4	3·0	24·3	—
Cl	Me	H	Me	I	108	68	EtOAc–Pet., 1	$C_8H_9O_3N_4Cl$	39·6	3·4	22·4	14·8	39·3	3·7	22·9	14·5
Cl	H	Me	Me	I	103	68	,,	$C_8H_9O_3N_4Cl$	39·1	3·8	23·4	14·7	39·3	3·7	22·9	14·5
Cl	H	H	Ph	I	173	60	,,	$C_{12}H_9O_3N_4Cl$	49·2	3·3	19·5	12·4	49·2	3·1	19·1	12·1
H	Cl	Ph	Ph	I	143	16	*n*-C_6H_{14}	$C_{18}H_{13}O_3N_4Cl$	58·5	3·5	15·0	9·8	58·6	3·5	15·2	9·6
Cl	H	Ph	Ph	I	156	45	EtOAc–Pet., 2	$C_{18}H_{13}O_3N_4Cl$	58·6	3·6	15·3	9·6	58·6	3·5	15·2	9·6
H	NEt_2	H	Me	II	—	—	—		Oil, but reduced directly							
H	$N<[CH_2]_4>O$	H	Me	II	144	61	MeOH	$C_{11}H_{15}O_4N_5$	47·0	5·5	24·6	—	47·0	5·3	24·9	—
NH_2	H	H	Me	II	216	77	Dioxan	$C_7H_9O_3N_5$	40·2	4·4	33·2	—	40·0	4·2	33·2	—
$CH_2Ph{\cdot}NH$	H	H	Me	II	162	88	EtOH	$C_{14}H_{15}O_3N_5$	55·7	4·9	22·9	—	55·8	5·0	23·3	—
Et_2N	H	H	Me	II	119	98	EtOAc–Pet., 2	$C_{11}H_{17}O_3N_5$	49·1	6·3	26·5	—	49·4	6·4	26·2	—
Me	OH	H	Me	(1)	238	—	$H{\cdot}CO{\cdot}NMe_2$	$C_8H_{10}O_4N_4$	42·5	4·1	24·4	—	42·5	4·4	24·7	—
Et_2N	Me	H	Me	II	118	77	EtOAc–Pet., 2	$C_{12}H_{19}O_3N_5$	51·5	6·6	24·5	—	51·2	6·8	24·9	—
$CH_2Ph{\cdot}NH$	H	H	Ph	II	189	94	Dioxan	$C_{19}H_{17}O_3N_5$	62·5	4·9	19·0	—	62·9	4·7	19·3	—
H	NH_2	Ph	Ph	(2)	194	—	,,	$C_{18}H_{15}O_3N_5$	61·4	4·4	20·4	—	61·9	4·3	20·1	—
H	NEt_2	Ph	Ph	II	177	86	EtOAc	$C_{22}H_{23}O_3N_5$	64·8	5·7	17·3	—	65·2	5·7	17·3	—
NH_2	H	Ph	Ph	II	219 ‡	62	EtOH	$C_{18}H_{15}O_3N_5$	61·9	4·2	20·0	—	61·9	4·3	20·1	—
Et_2N	H	Ph	Ph	II	180	84	EtOAc	$C_{22}H_{23}O_3N_5$	65·4	5·6	17·2	—	65·2	5·7	17·3	—
H	$CHPhBz{\cdot}NH$	Ph	Ph	(3)	194	—	Pet., 3	$C_{32}H_{25}O_4N_5$	70·7	4·6	12·9	—	70·7	4·6	13·0	—

* (1) Hydrolysis of the 6-chloro-compound in moist air. (2) Method II, without isolation of the 6-chloro-compound. (3) By-product from the 6-chloro-compound.

† Pet. = light petroleum: 1, b. p. 40—60°; 2, b. p. 60—80°; 3, b. p. 80—100°. ‡ With decomp.

TABLE II.

7 : 8-*Dihydropteridines* (III).

					Yield,			Found, %.			Required, %.			Absorption in 0·1N-HCl, λ (mμ.) (ε in parentheses).	
A.	B.	R.	R′.	M. p.	%.	Solvent.†	Formula.	C.	H.	N.	C.	H.	N.	Max.	Min.
H	NEt_2	H	Me	125°	*a*	MeOH	$C_{11}H_{17}N_5$	60·0	7·6	32·0	60·2	7·8	32·0	230 (14,400), 343 (12,000)	280 (1,800)
H	NEt_2	Me	Me	109	—	H_2O	$C_{12}H_{19}N_5$	62·1	7·7	29·7	61·8	8·1	30·0	—	—
H	$N<[CH_2]_4>O$	H	Me	152	72	C_6H_6	$C_{11}H_{15}ON_5$	56·7	6·3	30·0	56·7	6·4	30·0	247 (15,000), 305 (12,300)	280 (5,300)
H	NH_2	Ph	Ph	266	79	EtOH	$C_{18}H_{15}N_5$	71·4	4·9	22·8	71·8	5·0	23·2	257 (25,400), 370 (9,300)	315 (1,700),
H	NEt_2	Ph	Ph	168	67	EtOAc–Pet., 3	$C_{22}H_{23}N_5$	73·3	6·4	19·4	73·9	6·4	19·6	230 (23,800), 265 (21,300), 310 (13,100), 385 (11,000)	250 (18,000), 290 (10,500), 334 (3,500)
NH_2	H	H	Me	240 *	65	H_2O	$C_7H_9N_5$	51·3	5·4	43·2	51·5	5·6	42·0	290 (7,400)	260 (3,700)
Et_2N	H	H	Me	158	70	MeOH	$C_{11}H_{17}N_5$	60·0	7·6	32·0	60·3	7·8	32·0	250 (8,500)	—
$CH_2Ph{\cdot}NH$	H	H	Ph	242	70	EtOH–dioxan	$C_{19}H_{17}N_5$	72·8	5·0	22·1	72·4	5·4	22·2	—	—
NH_2	H	Ph	Ph	246	71	EtOH	$C_{18}H_{15}N_5$	71·6	5·0	23·0	71·8	5·0	23·3	232 (24,700), 335 (13,800)	305 (8,400)
Et_2N	H	Ph	Ph	139	81	MeOH–H_2O	$C_{22}H_{23}N_5$	73·5	6·4	19·8	73·9	6·4	19·6	232 (27,800), 280 (13,300), 337 (15,300)	265 (11,300), 312 (8,400)
Et_2N	Me	H	Me	121	70	Pet., 2	$C_{12}H_{19}N_5$	61·9	8·1	29·7	61·8	8·2	30·0	—	—

* With decomp. *a* 65% from crude amino-ketone. † Pet., see Table I, footnote.

TABLE III.

Pteridines (*substituents as in* III).

A.	B.	R.	R′.	Method of prepn.	M. p.	Yield, %.	Solvent.	Formula.	Found, %. C.	Found, %. H.	Found, %. N.	Required, %. C.	Required, %. H	Required, %. N.	Absorption in 0·1N-HCl, λ (mμ.) (ε in parentheses). Max.	Absorption in 0·1N-HCl, λ (mμ.) (ε in parentheses). Min.
NH_2	H	H	Me	IVa	>250° *	50	H_2O	$C_7H_7N_5$	51·9	4·4	44·0	52·2	4·3	43·5	235 (9,300), 305 (6,400)	265 (1,800)
NH_2	H	Ph	Ph	IVa IVb	244	94	EtOH	$C_{18}H_{13}N_5$	72·6	4·2	23·0	72·2	4·3	23·4	275 (12,900), 335 (14,800)	255 (10,500), 320 (6,600)
Et_2N	H	Ph	Ph	IVa	147	57	Pet., 2	$C_{22}H_{21}N_5$	74·2	6·2	19·9	74·4	5·9	19·7	230 (29,300), 273 (14,600), 335 (14,800)	260 (12,900), 305 (8,600)
H	NH_2	Ph	Ph	IVa IVb	210	90 5	MeOH–EtOAc	$C_{18}H_{13}N_5$	72·0	4·5	23·4	72·2	4·3	23·4	278 (12,800), 375 (15,100)	265 (10,700), 325 (6,100)
H	NEt_2	H	H	IVb	112	40	Pet., 2	$C_{10}H_{13}N_5$	59·1	6·2	34·0	59·1	6·4	34·5	228 (14,100), 340 (12,800)	280 (8,900)
Picrate					169		H_2O	$C_{16}H_{16}O_7N_8$	44·0	3·9	25·5	44·4	3·7	25·9		
H	NEt_2	Me	Me	IVa IVb	85	75 50	n-C_6H_{14}	$C_{12}H_{17}N_5$	62·0	7·3	30·5	62·3	7·4	30·3	235 (15,500), 340 (14,800)	280 (1,700)
H	NEt_2	Ph	Ph	IVa IVb	158	66 52	MeOH–H_2O	$C_{22}H_{21}N_5$	74·0	6·0	20·2	74·4	5·9	19·7	395 (22,700)	270 (9,000)
H	NEt_2	p-C_6H_4Cl	p-C_6H_4Cl	IVb	162	9	EtOH	$C_{22}H_{19}N_5Cl_2$	62·3	4·5	16·2†	62·2	4·5	16·5	—	—
H	NEt_2	7 : 8-Acenaphthylenylene		IVb	248	75	C_6H_6	$C_{20}H_{17}N_5$	73·4	5·0	21·0	73·4	5·2	21·4	282 (14,600), 340 (29,000)	260 (11,200), 300 (11,500)
H	NEt_2	9 : 10-Phenanthrylene		IVb	185	89	C_6H_6	$C_{22}H_{19}N_5$	74·9	5·4	19·9	74·8	5·4	19·8	235 (42,700), 305 (11,400) 412 (13,500)	285 (9,700), 345 (2,900)
H	NEt_2	2-Furyl	2-Furyl	IVb	164	50	MeOH	$C_{18}H_{17}O_2N_5$	64·1	4·8	20·9	64·5	5·1	20·9	—	—

* With decomp. † Found: Cl, 16·0. Reqd.: Cl, 16·7%.

(b) *Condensation of a* 4 : 5-*diaminopyrimidine with an* α-*diketone.* 5 : 6-Diamino-4-diethylaminopyrimidine (3·5 g.), benzil (4·5 g.), and ethanol (100 c.c.) were heated under reflux for 24 hours. After removal of the ethanol the residue was dissolved in dilute hydrochloric acid, and the solution extracted with light petroleum and basified with aqueous sodium hydroxide. The precipitated solid was collected and crystallised from aqueous methanol, giving 4-diethylamino-6 : 7-diphenylpteridine (3·6 g.), m. p. 157—158° (Found : C, 74·0; H, 6·0; N, 20·2. $C_{22}H_{21}N_5$ requires C, 74·4; H, 5·9; N, 19·7%).

For other pteridines prepared see Table III.

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