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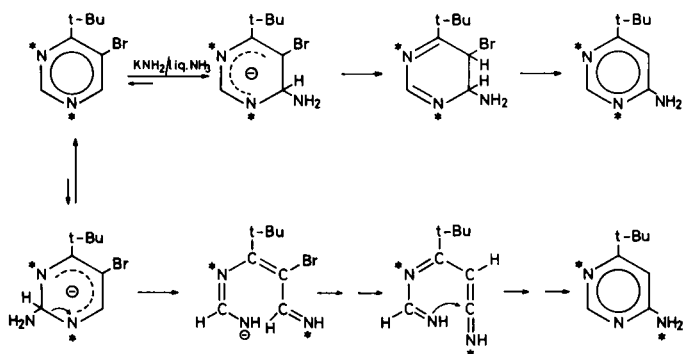
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The *cine*-amination of some 4-R-5-bromopyrimidines (*t*-butyl, phenyl, methoxyl, piperidine, methyl, methylamino, anilino, amino) by potassium amide in liquid ammonia has been studied. Evidence is presented that the conversion into the corresponding 4-substituted-6-aminopyrimidines can proceed in part *via* an $S_N(\text{ANRORC})$ mechanism, involving an open-chain intermediate, provided that the substituent at C-4 does not contain an acidic proton in the α -position to the pyrimidine ring. 5-Bromo-4-piperidinopyrimidine yields the *tele*-amination product, 2-amino-4-piperidinopyrimidine, alongside the 6-amino derivative. It is proven that the *tele*-amination does not proceed *via* an $S_N(\text{ANRORC})$ mechanism.

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Introduction.

Recently a detailed investigation into the mechanism of the *cine*-substitution of 5-bromo-4-*t*-butylpyrimidine (**1a**) (3) was published. ^{15}N -Labelling experiments proved that the reaction proceeds *via* two different mechanisms, as summarized in Scheme 1.



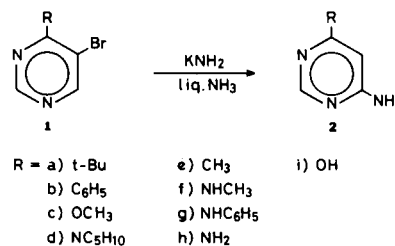
Scheme 1

A portion of the 6-amino-4-*t*-butylpyrimidine (**2a**) (49%) is formed *via* a mechanism involving an attack of the nucleophile on C-2, followed by ring opening, loss of hydrogen bromide and ring closure ($S_N(\text{ANRORC})$). The remainder is derived from the 1:1 σ -adduct (4) on C-6 by protonation and subsequent loss of hydrogen bromide. As shown in Scheme 1, using 5-bromo-4-*t*-butyl[1-(3)- ^{15}N]-pyrimidine as the substrate, the label is completely retained within the ring in the latter pathway and partially located on the exocyclic amino group in the $S_N(\text{ANRORC})$ process. More recently the open-chain mechanism received additional support by the observation that introduction of a *t*-butyl group at C-2 effectively blocks this pathway in the *cine*-substitution of 5-bromo-2,4-di-*t*-butylpyrimidine (5). It was therefore of interest to extend the investigations to 5-bromopyrimidines **1** with substituents other than a *t*-butyl group at C-4. A number of these compounds are known to undergo *cine*-substitution

upon reaction with potassium amide (6,7). A mechanism involving a "hetaryne" has been tentatively proposed. Pmr investigations (4) have since given rise to doubts as to the validity of this mechanism. Therefore, an investigation in greater detail was started with the prime objective to ascertain whether the substituent on C-4 influences the reaction mechanism to any great extent.

Results and Discussion.

Treatment of the 5-bromopyrimidines **1a-1i** with four equivalents of potassium amide in liquid ammonia at -33° slowly gave the corresponding 6-aminopyrimidines **2a-2i** as major reaction products (Scheme 2).



Scheme 2

The reaction times, identified products and yields are summarized in Table I. A varying amount of unidentifiable tar is also obtained in some cases, especially with substrates **1d** and **1e**.

In order to establish whether an $S_N(\text{ANRORC})$ mechanism is operative in these conversions the reactions were studied with two different ^{15}N -labelling techniques. The substrates **1a-1c** and **1h** were enriched with ^{15}N in the pyrimidine ring, the label being scrambled over the N-1 and N-3 atoms, and treated with unlabelled reagent (method A). Compounds **1d-1g** were reacted with ^{15}N -labelled potassium amide in ^{15}N -labelled ammonia (method B) (5,8). If ring opening takes place, ^{15}N will be present in the amino group of the products **2a-2c** and **2h** and will have been incorporated into the pyrimidine

Table I

Reaction Conditions and Products Obtained on Treatment of 4-R-5-Bromopyrimidines **1** with Potassium Amide in Liquid Ammonia

4-R-5-Bromo- pyrimidine 1	Mmoles of Substrate Employed	Reaction Time (Hours)	Retrieved Starting Material 1	Composition of Reaction Mixture (%)			
				4-R-6-Amino- pyrimidine 2	4-R- Pyrimidine	4-R-5-Bromo- 6-amino- pyrimidine	4-R-2-Amino- pyrimidine
1a (a) R = <i>t</i> -Bu	1	24	60	33	trace (b)	-	-
1b R = C ₆ H ₅	3	24	45	25	6-10 (b)	8 (d)	-
1c R = OCH ₃	1	24	21	75	- (c,d)	1-2 (d)	-
1d R = NC ₅ H ₁₀	0.5	48	10	40	1-2 (b)	trace (b)	4-6 (d)
1e R = CH ₃	0.5	72	10	50	1-2 (b)	-	-
1f R = NHCH ₃	0.5	48	30	48	-	-	-
1g R = NHC ₆ H ₅	0.5	72	10	67	3-4 (b)	-	-
1h R = NH ₂	1	24	60	30	trace (b,d)	-	-
1i R = OH	1	24	55	35	-	-	-

(a) *Viz* reference 3. (b) Identified by mass spectrometry. (c) Identified as 4-aminopyrimidine, see text. (d) Identified by independent synthesis.

Table II

Percent of Excess ¹⁵N in the Pyrimidines Involved in the *cine*-Substitution of **1a-1h** (a,b) and Percent of S_N(ANRORC) Mechanism in the Formation of **2a-2h**

Reaction Method	Starting Material 1	% Excess ¹⁵ N	4-R-6-Amino- pyrimidine 2	4-R-6-Halogeno- pyrimidine	% S _N (ANRORC)
A	1a (c)	7.3	7.3	5.5	49
A	1b	8.8	8.8	6.5	52
A	1c	7.9	7.8	6.8	26
B	1d	-	3.9	1.1	28
B	1e	-	4.1	0	0
B	1f	-	4.0	0	0
B	1g	-	4.0	0	0
A	1h	7.9	7.7	7.7 (d)	0

(a) Accuracy ± 0.2%. (b) All experiments were carried out in duplicate. (c) *Viz*. reference 3. (d) Measured as 4,6-dichloropyrimidine, see text.

ring of **2d-2g**. In order to establish this fact, the 6-aminopyrimidines **2a-2h** obtained were subsequently converted into the 6-halogeno derivatives. Acidic hydrolysis of compound **2b** followed by treatment with phosphoryl bromide afforded 6-bromo-4-phenylpyrimidine (**9**). Products **2a** (**3**) and **2c-2g** were diazotized in concentrated hydrochloric acid to yield the corresponding 6-chloropyrimidines. Both procedures have been reported as cited. A modification of the diazotization reaction, involving the use of cuprous chloride, enabled us to obtain some 4,6-dichloropyrimidine from **2h**. The excess of ¹⁵N contents in the 6-amino- and 6-halogenopyrimidines, and, when appropriate, the starting materials, were determined by mass spectrometry, by comparing the intensities of the M + 1 and M peaks. An S_N(ANRORC) mechanism is supported if a decrease in ¹⁵N enrichment is observed in

the 6-halogenopyrimidines obtained from **2a-2c** and **2h** and if any excess of ¹⁵N is found in the compounds formed from **2d-2g**. The values obtained are shown in Table II.

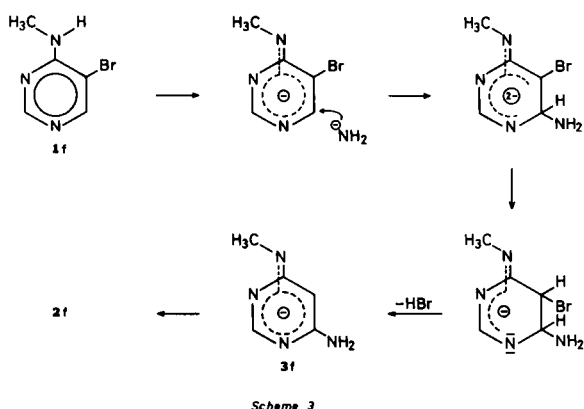
No product suitable for mass spectrometric analysis could be obtained from **2i** however, so the investigation of **1i** unfortunately had to be abandoned (**10**).

It is evident from the results in Table II that there is a remarkable difference between the compounds **1a-1d** compared to **1e-1h**. We will therefore discuss the results of both groups separately.

I. 4-R-5-Bromopyrimidines (**1e-1h**).

None of these compounds **1e-1h** are transformed into the 6-amino derivatives **2e-2h** via an S_N(ANRORC) process. They all have one characteristic in common however, *i.e.*, that the substituents on C-4 possess an acidic

hydrogen atom in a position adjacent to the pyrimidine ring. In the strongly basic potassium amide/liquid ammonia system this hydrogen atom can easily be abstracted to form an anion, the charge of which can be delocalized over the pyrimidine ring as exemplified in Scheme 3 for compound **1f**. Evidence for the existence of the anions of **1e** and **1f** had already been obtained from pmr studies (4). The pyrimidines **1g** and **1h** are insufficiently soluble in the potassium amide/liquid ammonia system to enable pmr measurements to be carried out (11). Since an essential step of the $S_N(\text{ANRORC})$ process is addition of an amide ion to C-2 of the pyrimidine ring, the data indicate that this route is apparently blocked by formation of an anion. Delocalisation of the negative charge leads to an enhanced electron density on the nitrogen atoms adjacent to C-2, thus causing a repulsion of an attack on that position by a negatively charged entity. Compounds **2e-2h** are formed *via* the process shown in Scheme 3 for the reaction of **1f**. The final step from **3f** probably takes place on quenching the reaction by the addition of ammonium chloride or nitrate.

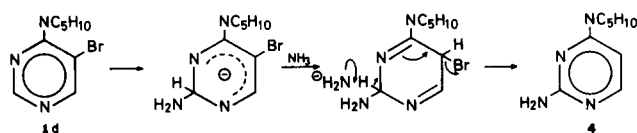


II. 4-R-5-Bromopyrimidines (**1a-1d**).

The remaining four pyrimidines **1a-1d** all undergo a nucleophilic *cine*-substitution *via*, to a certain extent, an open-chain intermediate. Compounds **1a-1c** have been found to give a 1:1 σ -adduct on C-6, as proven by pmr measurements. Compound **1d** is only slightly soluble in the reaction mixture, which makes it impossible to prove the existence of the σ -adduct, but it seems reasonable to assume that **1d** also forms a similar adduct (12,13). Since the $S_N(\text{ANRORC})$ process is initiated by addition to C-2 it is proposed that the attack of amide ion at C-2 occurs on the neutral substrate and not on the anionic σ -adduct at C-6. This possibility has been advanced earlier for the amination of **1a** in order to explain the low reaction rate (3).

Apart from the general pattern described above there are some interesting aspects of the conversion of **1b-1d** arising from the products formed alongside **2b-2d** (see Table I).

The reaction of **1d** is of special interest because of the formation of 2-amino-4-piperidinopyrimidine (**4**). This is the only example to date of the occurrence of a *tele*-amination in the 5-halogenopyrimidine series (14). The structure of **4** was proven by independent synthesis. 2,4-Dichloropyrimidine on treatment with piperidine yields 2-chloro-4-piperidinopyrimidine as the major product, as confirmed by reduction of the latter to 4-piperidinopyrimidine. Aminolysis of 2-chloro-4-piperidinopyrimidine with ethanolic ammonia gave 2-amino-4-piperidinopyrimidine. Compound **4** obtained from the reaction of **1d** with ^{15}N -labelled potassium amide was found to contain 3.7% of excess ^{15}N . After diazotization however, the isolated 2-chloro-4-piperidinopyrimidine contained no excess of ^{15}N at all, implying that an $S_N(\text{ANRORC})$ process is not involved in the formation of **4** from **1d**. In our earlier study on **1a** (3) we proved that the σ -adduct on C-6 cannot be involved in an $S_N(\text{ANRORC})$ process by cleavage of the N-1-C-6 bond since this would lead to the formation of 2-amino-4-*t*-butylpyrimidine, which is not found in the reaction mixture of **1a**. The fact that no ^{15}N is built into **4** in the reaction of **1d** is further support for the fact that the σ -adduct at C-6 is not involved in a ring-opening reaction since a process as described above would lead to incorporation of ^{15}N in the pyrimidine ring of **4**. The formation of **4** is excellent additional proof of attack occurring at C-2 in the reaction of **1d** with potassium amide. The mechanism proposed for the formation of **4** is depicted in Scheme 4.



When **1c** is treated with potassium amide in liquid ammonia, the dehalogenated product, 4-methoxypyrimidine, is not observed, but, rather a small amount of 4-aminopyrimidine is detected. Control experiments have shown that 4-methoxypyrimidine is completely converted into 4-aminopyrimidine under the conditions employed for the reaction of **1c** (15).

The reaction of **1b** deserves further attention due to the formation of an unusually high percentage of dehalogenated starting material 4-phenylpyrimidine (16). This product cannot be formed by dehalogenation of the starting material as such, since it was observed recently that 4-phenylpyrimidine is converted into a mixture of 2-amino-4-phenyl- and 6-amino-4-phenylpyrimidine by potassium amide in liquid ammonia (17). Since no 2-amino-4-phenylpyrimidine is detected in the reaction mixture of **1b**, 4-phenylpyrimidine cannot be present either

and is presumably formed on quenching the reaction by addition of ammonium salts.

The possibility of dehalogenation at C-5 of the pyrimidine occurring under the reaction conditions studied, raised the question as to whether 6-amino-4-phenylpyrimidine (**2b**) could be obtained by dehalogenation of 6-amino-5-bromo-4-phenylpyrimidine, a side product in the reaction of **1b**. This idea can be rejected on the following grounds. When 6-amino-5-bromo-4-phenylpyrimidine is reacted with potassium amide under identical conditions as **1b**, 46% of starting material, 30% of **2b** and 9% of a third product is obtained, to which, based on mass *m/e* 264/266, the structure of 5-bromo-2,4-diamino-6-phenylpyrimidine was tentatively assigned. However, careful investigation of the reaction mixture of **1b** by mass spectrometry showed that no trace of this compound with mass *m/e* 264/266 was present. This implies that 6-amino-5-bromo-4-phenylpyrimidine is excluded as a precursor of **2b** and that it is likely that just like 4-phenylpyrimidine, it is formed on quenching.

EXPERIMENTAL

Melting points are uncorrected. Mass spectra were recorded and excesses of ^{15}N were measured on an AEI MS 902 mass spectrometer. Column chromatography was carried out over Merck silica gel 60 (70-230 mesh ASTM). Pmr spectra were recorded in deuteriochloroform on a Hitachi-Perkin Elmer R-24B spectrometer.

Preparation of Starting Materials and Reference Compounds.

The following pyrimidines were prepared according to established procedures: 5-bromo-4-*t*-butyl-[1(3)- ^{15}N]pyrimidine (**1a**) (3), 5-bromo-4-methylpyrimidine (**1e**) (18), 5-bromo-4-*N*-methylaminopyrimidine (**1f**) (4), 6-amino-4-*t*-butylpyrimidine (**2a**) (18), 6-amino-4-phenylpyrimidine (**2b**) (18), 6-amino-4-methoxy-pyrimidine (**2c**) (19), 6-amino-4-piperidinopyrimidine (**2d**) (20), 6-amino-4-methylpyrimidine (**2e**) (18), 6-amino-4-*N*-methylaminopyrimidine (**2f**) (20), 6-amino-4-anilino-pyrimidine (**2g**) (20), 4,6-diaminopyrimidine (**2h**) (21), 6-amino-pyrimidin-4-one (**2i**) (21), 4-*t*-butyl-6-chloropyrimidine (18), 6-bromo-4-phenylpyrimidine (9), 6-chloro-4-methoxy-pyrimidine (22), 6-chloro-4-piperidinopyrimidine (20), 6-chloro-4-methylpyrimidine (18), 6-chloro-4-*N*-methylaminopyrimidine (23), 4-anilino-6-chloropyrimidine (24), 4,6-dichloropyrimidine (25), 4-methoxy-pyrimidine (26), 4-amino-pyrimidine (21), 5-bromo-4-chloropyrimidine (27), 5-bromo-6-chloro-4-phenylpyrimidine (18) and 2,4-dichloropyrimidine (28). 5-Bromo-4-phenyl-[1(3)- ^{15}N]pyrimidine (18), 5-bromo-4-methoxy-[1(3)- ^{15}N]pyrimidine (29), 4-amino-5-bromo-[1(3)- ^{15}N]pyrimidine (27) and 5-bromo-[1(3)- ^{15}N]pyrimidin-4-one (27) were synthesized as described for the respective unlabelled compounds **1b**, **1c**, **1h** and **1i**.

5-Bromo-4-piperidinopyrimidine (**1d**).

A solution of 2.0 g. (23.5 mmoles) of piperidine in 4 ml. of absolute ethanol was added at 0° with stirring to a solution of 1.5 g. (7.7 mmoles) of 5-bromo-4-chloropyrimidine (27) in 6 ml. of absolute ethanol. After 72 hours at 0° the precipitate was filtered off and the filtrate evaporated. The residue was extracted with 60 ml. of ether. The ethereal extract was dried over anhydrous magnesium sulphate, filtered and evaporated. The residual oil

was purified by distillation *in vacuo* to give 1.0 g. (54%) of **1d**, b.p. 164°/18 mm; ms: M^+ (*m/e*) 241/243; pmr: δ 8.43 (s, 1H), 8.30 (s, 1H), 3.60 (m, 4H), 1.66 (m, 6H). The picrate had m.p. 148-149° (from ethanol).

Anal. Calcd. for $\text{C}_{15}\text{H}_{15}\text{BrN}_6\text{O}_7$ (picrate 471.23): C, 38.23; H, 3.21. Found: C, 38.3; H, 3.1.

4-Anilino-5-bromopyrimidine (**1g**).

A solution of 1.5 g. (16 mmoles) of freshly distilled aniline in 6 ml. of absolute ethanol was added at 0° with stirring to a solution of 1.5 g. (7.7 mmoles) of 5-bromo-4-chloropyrimidine (27) in 12 ml. of absolute ethanol. After 72 hours at 0° the solvent was evaporated and the residue was extracted with 80 ml. of ether. The precipitate was filtered off and the filtrate was evaporated to dryness to give 1.8 g. (94%) of **1g** as a pale yellow oil that slowly solidified on standing, m.p. 68-70°; ms: M^+ (*m/e*) 249/251.

Anal. Calcd. for $\text{C}_{10}\text{H}_8\text{BrN}_3$ (250.10): C, 48.02; H, 3.23. Found: C, 47.9; H, 3.0.

6-Amino-5-bromo-4-phenylpyrimidine.

5-Bromo-6-chloro-4-phenylpyrimidine (18) (190 mg.; 0.7 mmole) was heated with 10 ml. of ethanolic ammonia saturated at 0° for 24 hours in a sealed tube at 140°. After evaporation of the solvent the residue was extracted with 40 ml. of cold chloroform. The chloroform was evaporated to give 164 g. (94%) of 6-amino-5-bromo-4-phenylpyrimidine. An analytical sample was obtained by column chromatography (silica gel, chloroform) to give m.p. 179-180°.

Anal. Calcd. for $\text{C}_{10}\text{H}_8\text{BrN}_3$ (250.10): C, 48.02; H, 3.23. Found: C, 48.2; H, 3.4.

6-Amino-5-bromo-4-methoxy-pyrimidine.

6-Amino-4-methoxy-pyrimidine (**2c**) (19) (350 mg.; 2.8 mmoles) was refluxed for 3 hours with 540 mg. (3.0 mmoles) of *N*-bromosuccinimide in 15 ml. of carbon tetrachloride. The precipitate was filtered off and the filtrate evaporated to dryness. The residue was crystallized from water to give 194 mg. (25%) of crude product, m.p. 155-160°. An analytical sample was obtained by column chromatography (silica gel, chloroform) to give m.p. 158-160°.

Anal. Calcd. for $\text{C}_5\text{H}_6\text{BrN}_3\text{O}$ (204.04): C, 29.43; H, 2.96. Found: C, 29.1; H, 2.8.

2-Chloro-4-piperidinopyrimidine.

2,4-Dichloropyrimidine (28) (1.3 g.; 10.1 mmoles) was refluxed for 1 hour with 1.8 g. (21.2 mmoles) of piperidine in 50 ml. of chloroform. After evaporation of the solvent the residue was extracted with 100 ml. of ether. The ether was evaporated and the product obtained was purified by column chromatography (silica gel, chloroform) to give 1.2 g. (61%) of 2-chloro-4-piperidinopyrimidine, m.p. 79-80°.

Anal. Calcd. for $\text{C}_9\text{H}_{12}\text{ClN}_3$ (197.67): C, 54.68; H, 6.12. Found: C, 54.8; H, 6.4.

4-Piperidinopyrimidine.

A mixture of 200 mg. (1.0 mmole) of 2-chloro-4-piperidinopyrimidine, 40 mg. of magnesium oxide, 40 mg. of palladium-charcoal catalyst and 50 ml. of methanol was shaken with hydrogen for 1 hour. The solvent was evaporated after filtration and the residue was purified by column chromatography (silica gel, chloroform) to give 60 mg. (37%) of 4-piperidinopyrimidine, m.p. 46-48°; pmr: δ 8.49 (s, 1H), 8.07 (d, 1H), 6.43 (d, 1H), 3.57 (m, 4H), 1.64 (m, 6H), $J_{5,6} = 6$ Hz.

Anal. Calcd. for $\text{C}_9\text{H}_{13}\text{N}_3$ (163.22): C, 66.23; H, 8.03. Found: C, 66.0; H, 8.4.

2-Amino-4-piperidinopyrimidine (4).

2-Chloro-4-piperidinopyrimidine (200 mg.; 1.0 mmole) was heated with 10 ml. of ethanolic ammonia saturated at 0° in a sealed tube for 24 hours. After evaporation of the solvent the residue was treated with a saturated solution of sodium bicarbonate and extracted with 150 ml. of chloroform. The chloroform was dried over anhydrous magnesium sulphate, filtered and evaporated. The product was purified by column chromatography (silica gel, ethyl acetate) to give 156 mg. (88%) of 4, m.p. 133-134°; pmr: δ 7.82 (d, 1H), 5.95 (d, 1H), 3.56 (m, 4H), 1.65 (m, 6H), $J_{5,6} = 6$ Hz.

Anal. Calcd. for $C_9H_{14}N_4$ (178.23): C, 60.65; H, 7.92. Found: C, 60.4; H, 8.0.

Amination Procedures.

The procedures for the amination reactions have been reported in previous papers. For method A (substrates 1a, 1b, 1c and 1h) see reference 3, for method B (substrates 1d-1g) see references 5 and 8. The amination of 4-methoxypyrimidine was carried out by method A.

Conversion of 4-R-6-Aminopyrimidines into 4-R-6-Halogenopyrimidines.

The conversion of 6-amino-4-phenylpyrimidine (2b) into 6-bromo-4-phenylpyrimidine is described in the literature (9). The 4-R-6-aminopyrimidines 2c-2g were diazotized into the corresponding 6-chloropyrimidines as described for the conversion of 2a (3). A similar procedure was followed for the diazotization of 2-amino-4-piperidinopyrimidine (4) into 2-chloro-4-piperidinopyrimidine. Purifications, when necessary, were carried out by column chromatography over silica gel, using chloroform, ethyl acetate or mixtures of these as eluents.

Diazotization of 4,6-Diaminopyrimidine (2h).

4,6-Diaminopyrimidine (2h) (45 mg.; 0.4 mmole) was dissolved in 2 ml. of concentrated hydrochloric acid. A solution of 0.5 g. (7.3 mmoles) of sodium nitrite in 2 ml. of water was added dropwise with stirring, maintaining the temperature between -15 and -20°. After the addition 5 ml. of a solution of freshly prepared cuprous chloride in concentrated hydrochloric acid were added at -10°. The stirring was continued at room temperature for 2 hours after which the reaction mixture was neutralized with concentrated ammonia and extracted with 50 ml. of ether. The ethereal extract was dried over anhydrous magnesium sulphate, filtered and evaporated to yield 1-2 mg. of 4,6-dichloropyrimidine.

Acknowledgments.

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- (10) It has been reported in the literature that 2i yields 4-amino-5-nitrosopyrimid-6-one on diazotization with sodium nitrite in formic acid. Kyowa Fermentation Co. Ltd., French Patent 1,415,149 (1965); *Chem. Abstr.*, 64, 5116b (1966).
- (11) Support for the existence of the anion of 1g is found in the ^{13}C -nmr spectrum of a solution of 2-anilino-4-chloropyrimidine in potassium amide in liquid ammonia. Although similar solubility problems are encountered the data indicate that the substrate is present as an anion. Cf. J. P. Geerts, H. C. van der Plas and A. van Veldhuizen, *Org. Magn. Reson.*, 7, 86 (1975).
- (12) This assumption is supported by the fact that the ^{13}C -nmr spectrum of 5-bromo-2-piperidinopyrimidine in a suspension of potassium amide in liquid ammonia shows signals that can only be ascribed to a similar adduct at C-6, viz reference 11.
- (13) The pmr spectrum of 1e, besides showing the signals of the anion (Section I), also shows the presence of a σ -adduct on C-6 in the reaction mixture, albeit in a smaller amount (3:1), viz reference 4.
- (14) Recently strong indications have been obtained that a similar *tele*-amination occurs on treatment of 5-bromo-4-*N,N*-dimethylaminopyrimidine with potassium amide in liquid ammonia. This substrate was not investigated in detail owing to very poor reproducibility of the reaction. Considerable amounts of tar are obtained.
- (15) This amino-demethoxylation has also been observed in this laboratory with other 4-methoxy derivatives, i.e., the formation of 4-amino-5-chloropyrimidine from 5-chloro-4-methoxypyrimidine, of 4-amino-6-methoxypyrimidine (2c) from 4,6-dimethoxypyrimidine and of 4-amino-5-bromo-6-methoxypyrimidine from 5-bromo-4,6-dimethoxypyrimidine.
- (16) Considerable dehalogenation has also been observed on treatment of 5-bromo-6-halogeno-4-phenylpyrimidines with potassium amide in liquid ammonia. Viz. J. de Valk and H. C. van der Plas, *Rec. Trav. Chim.*, 92, 145 (1973); J. de Valk, H. C. van der Plas and J. W. A. de Bode, *ibid.*, 92, 442 (1973).
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