[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS]

RESEARCHES ON PYRIMIDINES: CERTAIN DERIVATIVES OF 2-METHYLPYRIMIDINE[1]

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Among the more commonly utilized methods for the production of pyrimidine derivatives are interaction of (a) ureas with malonic esters (1) or β-diketones (2) and (b) amidines with β-keto esters (3), β-diketones (4), or cyanoacetates (5). The obviously closely related interaction of malonic esters with amidines has been but little studied since its initial use in 1922 (6). Seemingly, only ethyl malonate and five straight chain-alkylmalonic esters have thus been converted into 5-*n*-alkyl-2-methyl-4,6(1,5)-pyrimidinediones (7, 8).[4] Conversion of the latter into other pyrimidine derivatives has not been recorded.

In the present investigation, acetamidine has been condensed with malonic ester and eight ethyl alkylmalonates to form a series of 2-methylpyrimidinediones. The latter, which include two compounds possessing branched chain alkylation, have been converted into the corresponding chloropyrimidones and dichloropyrimidines. Although these dichloro derivatives react readily with ammonia, the halogen is not replaced by hydrogen, as anticipated, through exposure to zinc dust and boiling water. However, catalytic hydrogenolysis of the 4-amino-6-chloropyrimidines to the aminopyrimidines was accomplished.

Using phenol as a reaction medium, the dichloro compounds were converted into dianilino derivatives. Attempts to prepare Grignard reagents from the dichloropyrimidines[5] were unsuccessful. When ethyl bromide and the dichloropyrimidines were mixed and added to magnesium, some replacement of the halogens by ethyl groups was observed.[6]

[1] From the Ph.D. dissertations of William Josiah Clegg (June, 1947) and Charles William Smart (June, 1950).

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[4] The title of this article is "A Series of 2-Methyl-5-alkyl-4,6-dihydroxypyrimidines". The compounds are listed in the Subject Index of "Chemical Abstracts" as 4,6-pyrimidiols, rather than as pyrimidinediones, although the interpretation of the ultraviolet absorption spectra does not substantiate the diol structure.

[5] A paper by W. Proost and J. P. Wibaut [*Rec. trav. chim.*, **59**, 976 (1940)] suggested the possibility of the formation of Grignard reagents with dichloropyrimidines. These investigators showed that simultaneous addition of 2,6-dibromopyridine with ethyl bromide to a reacting mixture of ethyl bromide and magnesium resulted in the formation of pyridine-2,6-dimagnesium bromide. If this interaction could be adapted to dichloropyrimidines an interesting new tool for the synthesis of pyrimidine derivatives would be available.

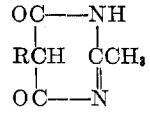
[6] In *no* case was replacement of chlorine by ethyl successful unless a stainless steel stirrer was present; this fact implies that the interchange is catalyzed either by a metallic surface or by salts of metals.

EXPERIMENTAL

Preparation of 5-alkyl (or *hydrogen*)*-2-methyl-4,6(1,5)-pyrimidinediones.* The method of Kenner, Lythgoe, Todd, and Tophan (9) was modified as follows: Sodium (69 g., 3 gram-atoms) was dissolved in 1 l. of cooled ethanol; acetamidine hydrochloride (94.5 g., 1 mole) was added and the resulting precipitate of sodium chloride was removed. To the briskly stirred filtrate was added ethyl malonate or a monoalkylmalonate (1 mole), and the closed container was kept for 24–48 hours while another precipitate formed. The mixture was chilled, filtered, and the solid material was dissolved in a liter of water. Addition of concentrated hydrochloric acid caused precipitation of the pyrimidinedione. Dilution of the filtrate with two volumes of water and addition of more acid produced further precipitation of dione. Purification was accomplished through dissolution of the dione in concentrated ammonium hydroxide, filtration, and boiling the solution to reprecipitate the pyrimidi-

TABLE I

DERIVATIVES OF 2-METHYL-4,6(1,5)-PYRIMIDINEDIONES



R	YIELD, %	CARBON		HYDROGEN		NITROGEN	
		Calc'd	Found	Calc'd	Found	Calc'd	Found
H	87.2[a]	47.62	47.51	4.80	4.84		
CH_3	71.2[b]	51.42	51.49	5.75	5.59	19.98	19.91
C_2H_5	73.0[c]	54.52	54.54	6.54	6.42	18.18	18.17
C_3H_7	61.0[d]					16.66	16.71
C_4H_9	91.8[e]	59.32	59.82	7.74	7.96	15.37	15.30
$CH(CH_3)C_2H_5$	76.0	59.32	59.19	7.74	7.80	15.37	15.20
$CH_2CH(CH_3)_2$	60.0	59.32	59.20	7.74	7.62	15.37	15.30
C_5H_{11}	81.5[f]	61.20	61.11	8.22	8.37	14.27	14.30
C_6H_{13}	85.8	62.83	62.44	8.63	8.68	13.33	13.05

[a] Dox and Yoder, (6) reported 62% yield; Ferris and Ronzio (8) reported 43% yield. [b] Huber and Hölscher (7) reported 58% yield; Ferris and Ronzio (8) reported 18% yield. [c] Ferris and Ronzio (8) reported 15% yield. [d] Ferris and Ronzio (8) reported 22% yield. Remfry [*J. Chem. Soc.*, **99**, 610 (1911)] made the initial report of the synthesis of this compound from interaction of propylmalonamide and ethyl malonate but omitted the yield. [e] Ferris and Ronzio (8) reported 33% yield. [f] Ferris and Ronzio (8) reported 26% yield.

nedione. The melting points of the pyrimidinediones are above 360°. Commercial methanol and 96% sodium methoxide[7] could be used without decreasing the yield of the pyrimidinediones. Analytical data for these products are listed in Table I.

Preparation of derivatives of 4,6-dichloro-2-methylpyrimidine. One equivalent of a finely ground 4,6(1,5)-pyrimidinedione was mixed with six equivalents of phosphorus oxychloride and heated to gentle reflux for about two hours, causing evolution of hydrogen chloride; then the temperature was raised causing fresh gas evolution. Most of the excess phosphorus oxychloride was removed by distillation under a partial vacuum. The residual liquid material was poured onto a large amount of crushed ice and the oily, or semi-solid product was removed; the aqueous solution was extracted with ether. After being dried over sodium sulfate, the extracts were freed from ether and the residue was combined with

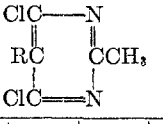
[7] Mathieson Chemical Corporation, Niagara Falls, N. Y.

the main portion of the product. The latter was chilled to cause precipitation of a small amount of 2,5-dialkyl-6-chloro-4(3)-pyrimidone. The dichloropyrimidines were purified by fractional distillation under diminished pressure. No advantage was evident in this preparation as a result of the addition of phorphorus pentachloride to the phosphorus oxychloride.

Alternately, the ether solution of a reaction product was extracted with 5% sodium hydroxide solution. Acidification of the alkaline extract yielded the chloropyrimidone. Benzene proved to be the most suitable solvent for recrystallization of these mono-chloro derivatives. In one experiment, 4,6-dichloro-2-methylpyrimidine was dissolved in alcohol, treated with 2.5 *N* hydrochloric acid, and heated to remove the alcohol. Some solid material had appeared, so water was added and the mixture was boiled for an hour. The solid product was removed, and recrystallized from benzene to give 39% of purified 6-chloro-2-methyl-4(3)-pyrimidone. The 5-methyl- and 5-ethyl-4,6-dichloro-2-methylpyrimidines were par-

TABLE II

DERIVATIVES OF 4,6-DICHLORO-2-METHYLPYRIMIDINE



R	B.P., °C. (corr.)	MM.	YIELD, %	n_D^{25}	d_4^{25}	MOLECULAR REFRAC.		CHLORINE		NITROGEN	
						Σ^d	Calc'd	Calc'd	Found	Calc'd	Found
H[a]	46–48[b]		74.7								
CH_3	38–39[c]		60.1							15.83	15.80
C_2H_5	100–101	10	59.7	1.5289	1.2645	46.82	46.59	37.12	36.52	14.67	14.64
C_3H_7	114–115	11	48.6	1.5217	1.2209	51.44	51.21			13.66	13.62
C_4H_9[e]	113–114	4	51.4	1.5172	1.1831	56.05	56.04	32.36	32.29	12.79	12.78
$CH(CH_3)C_2H_5$	88–89	2	68.2	1.5144	1.1787	56.05	56.07			12.79	12.72
$CH_2CH(CH_3)_2$	91–92	6	77.2	1.5148	1.1780	56.05	56.04			12.79	12.75
C_5H_{11}	109–110	3	61.3	1.5126	1.1517	60.67	60.70	30.42	30.28	12.02	11.97
C_6H_{13}	134.0–134.7	5	68.0	1.5099	1.1286	65.29	65.49	28.69	28.38		

[a] Baddiley, Lythgoe, McNeil, and Todd [*J. Chem. Soc.*, 383(1943)] reported m.p. 48–49°. [b] Melting point of this compound. [c] Melting point of this compound; Huber and Hölscher (7) reported m.p. 39°. [d] Summation value includes value of 3.712 as atomic refraction for nitrogen in C—N=C. [e] *Anal.* Calc'd for $C_9H_{12}Cl_2N_2$: C, 49.33; H, 5.52. Found C, 49.13; H, 5.57.

tially hydrolyzed by boiling with 5% sodium hydroxide solution until the mixtures became homogeneous. After extractions with ether, the alkaline solutions were neutralized with glacial acetic acid, causing formation of amorphous products. The latter were dried, and recrystallized from benzene to give a 71% yield of 6-chloro-2,5-dimethyl-4(3)-pyrimidone and a 57% yield of the 5-ethyl homolog.

Data concerning the 4,6-dichloropyrimidines appear in Table II, and for the 6-chloro-4(3)-pyrimidones in Table III.

Preparation of derivatives of 4,6-diamino-2-methylpyrimidine. In general, about 0.03 mole of the 2,5-dialkyl-4,6-dichloropyrimidine was mixed in a Carius tube with 50 cc. of concentrated ammonium hydroxide solution. The tube was sealed and heated at 180–200° for nine hours. Upon cooling, the crystalline product was recovered and recrystallized from water solution. In the case of the dimethyl derivative, the product proved to be the monohydrochloride; from the latter the diamine was liberated by treatment with alkali. The

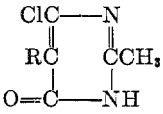
ethyl and hexyl members required treatment with alkali in their purification. Data concerning these diaminopyrimidines have been placed in Table IV.

Preparation of derivatives of 6-amino-2-methyl-4(3)-pyrimidone. The crystalline 6-chloro-2-methyl-4(3)-pyrimidone or homolog (0.014 mole) was introduced into a Carius tube together with concentrated ammonium hydroxide (25 ml.). After sealing, the tube was heated to 170–180° for nine hours. When cool, the tube was opened and the solid material was removed and recrystallized from dilute alcohol to yield coarse, white platelets. Appropriate data concerning these six derivatives may be found in Table V.

Preparation of derivatives of 6-amino-4-chloro-2-methylpyrimidine. In general, 0.03 mole of a 4,6-dichloro-2-methylpyrimidine was mixed in a Carius tube with 50 ml. of concentrated ammonium hydroxide; the tube was sealed and heated at 132–140° for nine hours. After cooling, the tube was opened and the reaction mixture (coarse, white crystals) was removed and recrystallized from dilute alcohol.

TABLE III

DERIVATIVES OF 6-CHLORO-2-METHYL-4(3)-PYRIMIDONE



R	M.P., °C. (corr.)	YIELD, %	CHLORINE		NITROGEN		CARBON		HYDROGEN	
			Calc'd	Found	Calc'd	Found	Calc'd	Found	Calc'd	Found
H[a]	231.5–232.0	39[b]	24.53	24.84	19.38	19.23				
CH_3	224.5–225.0	71[c]	22.36	22.21	17.66	17.64				
C_2H_5	207–208	57[c]	20.54	20.49	16.23	16.28	48.70	48.46	5.26	5.31
C_3H_7	220.3–221.3	2[d]	19.00	19.40						
C_4H_9	173.5–174.5	7[d]	17.66	17.83	13.96	13.91				
$CH(CH_3)C_2H_5$	124.3–125.3	3[d]	17.66	17.58	13.96	13.93	53.87	53.72	6.53	6.59
$CH_2CH(CH_3)_2$	167.5–168.5	1[d]			13.96	13.90				
C_5H_{11}	168–169	5[d]	16.51	16.49	13.05	12.94	55.94	55.67	7.04	7.09
C_6H_{13}	144–145	3[d]			12.25	12.57				

[a] This compound, prepared by heating 4,6-dichloro-2-methylpyrimidine with 10% hydrochloric acid, was reported as melting at 233° by Basford, Curd, and Rose, *J. Chem. Soc.*, 713 (1946). [b] This yield was obtained by hydrolysis of the dichloropyrimidine with boiling hydrochloric acid; hydrolysis with sodium hydroxide solution gave 24% yield. [c] This yield was obtained by hydrolysis of the dichloropyrimidine with boiling dilute sodium hydroxide solution. [d] Yield of monochloropyrimidone recovered from conversion of corresponding pyrimidinedione into dichloropyrimidine.

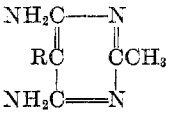
The conversion into the amino chloro compound occurred at temperatures much lower than 130°, but then was slow and incomplete; higher temperatures caused replacement of both chloro substituents by amino. Data for the melting points and from analyses of the six derivatives appear in Table VI.

Preparation of derivatives of 4-amino-2-methylpyrimidine. To prepare the catalyst, a mixture of palladium chloride, hydrochloric acid, methanol and activated charcoal was shaken with hydrogen, under 800 mm. pressure. To the catalyst was added a methanolic solution of 4-amino-6-chloro-2-methylpyrimidine, or a homolog; hydrogen was again introduced into the vessel and shaking begun. The calculated quantity of hydrogen was utilized in about 40 minutes, but agitation was continued for a half-hour. After filtration from the catalyst

and charcoal, the filtrate was heated to remove the alcohol and was treated either with concentrated ammonium hydroxide solution or 30% sodium hydroxide solution to precipi-

TABLE IV

DERIVATIVES OF 4,6-DIAMINO-2-METHYLPYRIMIDINE

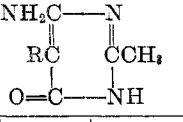


R	M.P., °C. (corr.)	YIELD, %	CARBON		HYDROGEN		NITROGEN		PICRATE		
			Calc'd	Found	Calc'd	Found	Calc'd	Found	M.p., °C., (corr.)	Nitrogen	
										Calc'd	Found
H[a]	303–304	55							288.5 (dec.)	27.76	27.03
CH_3[b,c]	234–235	46							293 (dec.)	26.70	26.78
C_2H_5	232–233	61	55.24	55.20	7.95	8.09			277–278 (dec.)	25.72	25.68
C_4H_9	151–152	66	59.97	60.01	8.95	9.14	31.09	30.73	225–226	23.95	23.54
C_5H_{11}	161.5–163.5	75	61.81	61.67	9.34	9.30			178.5–179.5	23.16	22.80
C_6H_{13}	149.0–149.5	88	63.42	63.10	9.68	9.96					

[a] Baddiley, Lythgoe, McNeil, and Todd [*J. Chem. Soc.*, 383 (1943)] reported m.p. 294–295°. [b] Huber and Hölscher [*Ber.*, **71,** 91 (1938)] reported m.p. 225–226° and a *picrate*, turning brown at 265° and decomposing at 285°. [c] A *hydrochloride* was obtained, m.p. 323–332° [Huber and Hölscher, *Ber.*, **71,** 91 (1938) reported m.p. 330°]; *Anal.* Calc'd for $C_6H_{10}N_4 \cdot HCl$: C, 41.27; H, 6.35. Found: C, 41.54; H, 6.50.

TABLE V

DERIVATIVES OF 6-AMINO-2-METHYL-4(3)-PYRIMIDONE



R	M.P., °C. (corr.)	YIELD, %	NITROGEN		CARBON		HYDROGEN	
			Calc'd	Found	Calc'd	Found	Calc'd	Found
H[a]	301 (dec.)	6.6	33.58	31.64				
CH_3	283.0–283.5	90.4	30.20	29.57	51.78	51.26	6.52	6.79
C_2H_5[b]	272.4–273.4	74			55.01	55.12	7.26	7.62
C_4H_9	261.5–262.5	77	23.19	23.31				
C_5H_{11}[c]	250–251	63.8			61.52	61.45	8.78	9.15
C_6H_{13}	240.4–241.4	65			63.12	62.99	9.15	9.37

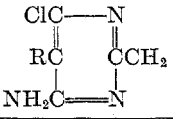
[a] Traube, German Patent 134,984, reported m.p. 298–300° (dec.); Fodi, Demjen, Szederes, and Halmos [*Ber.*, **75,** 755 (1943)] reported m.p. 293–294°. [b] A *picrate* was obtained, m.p. 227.5°; *Anal.* Calc'd: N, 21.99. Found: N, 22.21. [c] A *picrate* was obtained, m.p. 199.2–201.2°; *Anal.* Calc'd: N, 19.62. Found: N, 19.66.

tate the amino alkylated pyrimidines. The latter were recrystallized from hot benzene. Certain data for these aminopyrimidines may be found in Table VII.

Preparation of derivatives of 4,6-dianilino-2-methylpyrimidine. A mixture of 4,6-dichloro-2-methylpyrimidine, or of a homolog, (0.05 mole), aniline (0.11 mole), and phenol (50 g.)

TABLE VI

DERIVATIVES OF 4-AMINO-6-CHLORO-2-METHYLPYRIMIDINE

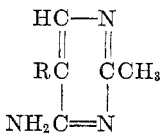


R	M.P., °C. (corr.)	YIELD, %	NITROGEN		CARBON		HYDROGEN		CHLORINE	
			Calc'd	Found	Calc'd	Found	Calc'd	Found	Calc'd	Found
H[a]	190–191[b]	87.6								
CH_3[c]	199.5–200.5[d]	65.6								
C_2H_5[e]	229.5–231.0	88.9	24.06	23.61	49.86	49.71	5.77	5.89	20.31	20.59
C_4H_9[f]	167.8–168.0	96.3	21.05	21.45	54.13	53.88	7.07	6.57	17.76	17.77
C_5H_{11}[g]	144.5–145.0	91.3	19.66	19.45	56.20	56.05	7.55	7.77	16.54	16.82
C_6H_{13}[h]	152–153	98.7			58.01	57.99	7.97	8.32	15.56	15.86

[a] Fodi, Fodor, Demjen, Szekeres, and Halmos [*Ber.*, **75,** 755 (1942)] reported m.p. "about 200°" for a *picrate*. In this study, the *picrate* melted at 198–199°; *Anal.* Calc'd: N, 22.55. Found: N, 22.32. [b] Baddiley, Lythgoe, McNeil and Todd [*J. Chem. Soc.*, 383 (1943)] reported m.p. 190–191°. [c] A *picrate* melted at 197.0–197.8°; *Anal.* Calc'd: N, 21.73. Found: N, 21.70. [d] Huber and Hölscher [*Ber.*, **71,** 91 (1938)] reported m.p. 196–197°. [e] A *picrate* melted at 212°; *Anal.* Calc'd: N, 20.97. Found: N, 21.08. [f] A *picrate* melted at 176.5–177.5°; *Anal.* Calc'd: N, 19.60. Found: N, 19.60. [g] A *picrate* melted at 183.6–184.6°; *Anal.* Calc'd: N, 18.98. Found: N, 19.10. [h] A *picrate* melted at 172.2–173.2°; *Anal.* Calc'd: N, 18.40. Found: N, 18.49.

TABLE VII

DERIVATIVES OF 4-AMINO-2-METHYLPYRIMIDINE



R	M.P., °C. (corr.)	YIELD, %	CARBON		HYDROGEN		NITROGEN	
			Calc'd	Found	Calc'd	Found	Calc'd	Found
H[a]	205.9–206.9	55						
CH_3[b]	205.4–206.4	92						
C_2H_5[c]	158.5–160.0	75	61.28	61.01	8.08	8.26	30.63	29.96
C_4H_9[d]	102.5–103.5	56	65.38	65.20	9.15	9.06	25.43	25.34
C_5H_{11}[e]	129.5–130.5	94	67.00	66.84	9.56	9.87		
C_6H_{13}[f]	119.2–119.7	97	68.35	68.57	9.91	10.02		

[a] Gabriel [*Ber.*, **37,** 3642 (1904)] reported m.p. 205°. [b] Williams, Ruehle, and Finkelstein, [*J. Am. Chem. Soc.*, **59,** 529 (1937)] reported m.p. 201–202°. [c] A *picrate* melted at 190–191°: *Anal.* Calc'd: N, 22.95. Found: N, 23.4. [d] A *picrate* melted at 185.0–185.5°; *Anal.* Calc'd: N, 21.31. Found: N, 21.45. [e] A *picrate* melted at 154.5–156.0°; *Anal.* Calc'd: N, 20.58. Found: N, 20.84. [f] A *picrate* melted at 133.7–134.7°; *Anal.* Calc'd: N, 19.90. Found: N, 20.10.

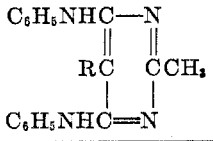
was heated to refluxing for ten hours. Alcohol (50 ml.) was added, and the solution poured into a sodium hydroxide (0.5 mole) solution (200 ml.), causing separation of an oily, liquid phase which eventually solidified. The solid material was removed and recrystallized from

alcohol. This procedure produced better yields than did one using an excess of aniline as solvent. Pertinent data for these anilino derivatives are listed in Table VIII.

Interaction of ethylmagnesium bromide and 4,6-dichloro-2-methylpyrimidines. Ethyl bromide (1 g.) in 20 ml. of anhydrous ether was added to 6 g. (0.25 gram-atom) of magnesium; reaction began at once. Now there was slowly added a solution of the 4,6-dichloro-2-methyl-

TABLE VIII

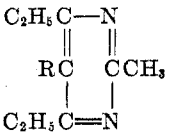
DERIVATIVES OF 4,6-DIANILINO-2-METHYLPYRIMIDINE



R	M.P. °C. (corr.)	YIELD, %	NITROGEN		CARBON		HYDROGEN		PICRATE		
			Calc'd	Found	Calc'd	Found	Calc'd	Found	M.P., °C. (cor.)	Nitrogen	
										Calc'd	Found
CH_3	194.5–195.5	79.3	19.29	19.36					194.5–195.5	18.88	18.93
C_2H_5	148–149	73.7	18.41	18.36	74.96	74.90	6.62	6.68	222–223	18.38	18.30
C_3H_7	146.0–146.5	89.4	17.60	17.55					189–190	17.91	17.87
C_4H_9	128–129	75.8	16.86	16.72					184–185	17.46	17.48
$CH(CH_3)C_2H_5$	91.5–92.5	85.4	16.86	16.80	75.87	75.91	7.28	7.33	198–199	17.46	17.44
$CH_2CH(CH_3)_2$	96–97	63.8	16.86	16.89					209–210	17.46	17.46
C_5H_{11}	113–114	82.1	16.17	16.14					142–144	17.04	16.98

TABLE IX

PICRATES OF DERIVATIVES OF 4,6-DIETHYL-2-METHYLPYRIMIDINE



R	M.P. °C. (corr.)	NITROGEN		CARBON		HYDROGEN	
		Calc'd	Found	Calc'd	Found	Calc'd	Found
CH_3	106–107	17.81	17.90				
C_2H_5	101–102	17.19	17.35				
C_3H_7	124–125	16.62	16.55				
C_4H_9	98–99	16.09	15.97				
$CH(CH_3)C_2H_5$	162–163	16.09	15.94				
$CH_2CH(CH_3)_2$	165–166	16.09	15.70	52.40	51.75	5.79	5.78
C_5H_{11}	171–172	15.58	15.51	53.44	53.34	6.05	6.04

pyrimidine, or homolog, (0.05 mole) and ethyl bromide (10 g., total of 0.1 mole) in 200 ml of dried ether; addition required 90 minutes. The stirred reaction mixture was maintained at gentle reflux temperature for about two hours longer, the color of the solution becoming darker to a red to brown color (if this color change did not occur, no replacement of halogen in the dichloropyrimidine was observed).

The reaction mixture was kept at room temperature for about nine hours before it was again heated to reflux before addition of methanol (0.25 mole); heating was continued for about an hour. The slurry was poured into 300 ml. of ice-water, the whole was acidified with 10% hydrochloric acid, and unreacted magnesium was quickly removed. The extract was dried and the solvent was removed *in vacuo* at room temperature. The residue was chiefly unreacted dichloropyrimidine and did not yield a solid picrate. The material was brought to *p*H 8-9 and was re-extracted with ether. This extract did form a picrate. In no case was it found possible to purify the 4,6-diethyl-2-methylpyrimidines by diminished pressure distillation, so these products were isolated as picrates. Data for these picrates are to be found in Table IX.

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