2,3-Cyclopenteno-7H-benzo[c] fluorene (II). To a solution of 2.5 g. of the foregoing ketone in 30 ml. of anhydrous xylene, 2.6 g. of finely powdered phosphorus pentoxide was added in small portions, and the mixture was refluxed for 30 hr. After cooling, water was added, and the dark fluorescent xylene solution was washed with aqueous sodium hydroxide, then with water, and dried over sodium sulfate; the solvent was then distilled off and the residue vacuum-fractionated. The thick yellow oil, b.p. 220–225°/0.4 mm. was taken up in ethanol containing some drops of benzene, and the solid precipitate obtained was recrystallized from ethanol, giving shiny colorless needles, m.p. 140° (no coloration with cold sulfuric acid). Yield: 30%.

Anal. Calcd. for $C_{20}H_{16}$: C, 93.7; H, 6.3. Found: C, 93.4; H, 6.3.

The corresponding picrate crystallized from ethanol in orange-red prisms, m.p. 184°.

Anal. Calcd. for $C_{26}H_{19}N_3O_7$: N, 8.7. Found: N, 8.4.

2-(1-Naphthylmethylene)-6,7-cyclopenteno-1-tetralone (IV). A solution of 0.35 g. of ketone III and 0.3 g. of 1-naphthaldehyde in 3 ml. of warm ethanol was treated with one drop of 20% aqueous potassium hydroxide; the solid precipitate formed on cooling crystallized from ethanol in shiny yellowish prisms (0.35 g.), m.p. 115°, giving a deep red halochromism with sulfuric acid.

Anal. Calcd. for $C_{24}H_{20}O$: C, 88.9; H, 6.2. Found: C, 88.6; H, 6.3.

Treatment of this ketone with phosphorus pentoxide in xylene as for the above hydrocarbon, afforded a compound which crystallized from a mixture of ethanol and benzene in shiny colorless leaflets, m.p. 249°, which gave no picrate.

5,6-Dihydro-2,3-cyclopenteno-11H-benzo[a]carbazole (V). A mixture of 3.5 g. of ketone III and 3 g. of phenylhydrazine was heated at 120° until steam had ceased to be evolved; on cooling, 30 ml. of acetic acid saturated with hydrogen chloride was added. The mixture was brought to the boil, poured into water, and the indolization product taken up in benzene; the benzene solution was washed with dilute aqueous sodium hydroxide, then with water, dried over sodium sulfate, the solvent removed, and the residue vacuum-distilled. The portion boiling above 250°/12 mm. crystallized from ethanol in colorless prisms (2.5 g.), m.p. 204°.

Anal. Calcd. for $C_{19}H_{17}N$: N, 5.4. Found: N, 5.2.

The corresponding picrate crystallized from ethanol in shiny, deep violet prisms, m.p. 194°.

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Selective Reduction of a Benzyloxyamino Group in the Presence of a Nitro Group[1]

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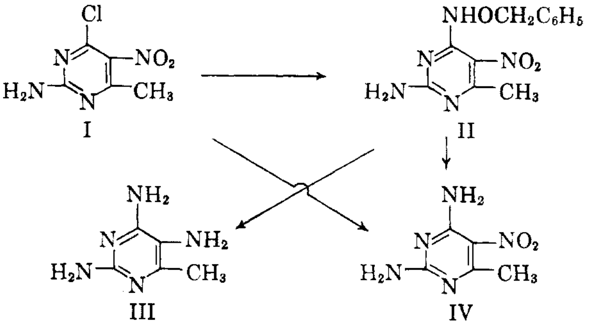
In the course of experiments directed towards the synthesis of purine-9-oxides, selective reduction of the nitro group in 2-amino-4-benzyloxyamino-5-nitro-6-methylpyrimidine (II) was attempted. This could not be achieved, but conditions have been found for the selective reduction of the benzyloxyamino group.



Reaction of II with hydrazine in the presence of Raney nickel, with ferrous hydroxide or with hydrogen in the presence of palladium catalyst resulted in complete reduction to 2,4,5-triamino-6-methylpyrimidine (III). Unexpectedly, however, reduction with aqueous ethanolic ammonium sulfide gave 2,4-diamino-5-nitro-6-methylpyrimidine (IV), identical with the reaction product of 2-amino-4-chloro-5-nitro-6-methylpyrimidine (I) with ethanolic ammonia.

The steric environment of the nitro group in II probably contributes to the selectivity of the latter reduction. These experiments emphasize the ease of reduction of the benzyloxy grouping under neutral or alkaline conditions where hydrolysis of the group does not occur.

EXPERIMENTAL[2]

2-Amino-4-benzyloxyamino-5-nitro-6-methylpyrimidine (II). To a solution of 9.5 g. of 2-amino-4-chloro-5-nitro-6-methylpyrimidine[3] in 200 ml. of ethanol was added 8.0 g. of benzyloxyamine[4] and 8.5 g. of powdered anhydrous sodium acetate. The mixture was heated under reflux for 1 hr., the solvent removed under reduced pressure and the residue triturated with water. The yellow solid which separated was collected by filtration and recrystallized from ethanol to give 12.0 g. (78%) of fine yellow needles, m.p. 191–192°.

Anal. Calcd. for $C_{12}H_{13}N_5O_3$: C, 52.4; H, 4.7; N, 25.45. Found: C, 52.6; H, 4.9; N, 25.3.

2,4,5-Triamino-6-methylpyrimidine (III). Method *a.* A suspension of 2 g. of powdered 2-amino-4-benzyloxyamino-5-nitro-6-methylpyrimidine in 200 ml. of ethanol was treated with 2 ml. of 96% hydrazine followed by a small amount of Raney nickel catalyst. The resulting mixture was heated under reflux for 20 min., filtered, and the filtrate evaporated to dryness. Recrystallization of the residue from ethanol yielded 0.65 g. (64%) of small tan prisms, m.p. 242–244°. This material is reported to melt at 243°[5] and 241–243°.[6]

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(1) This investigation was supported by a grant from the American Cancer Society.

(2) We are indebted to Dr. Joseph F. Alicino, Metuchen, N. J., for the microanalyses. All melting points are corrected.

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Method *b*. To a stirred solution of 18.5 g. of hydrated ferrous sulfate in 300 ml. of water at 75° was added 27 g. of hydrated barium hydroxide. After 15 min., 2 g. of powdered 2-amino-4-benzyloxyamino-5-nitro-6-methylpyrimidine was added, the mixture stirred, and the temperature raised to 100° for 20 min. The hot solution was filtered and the filter cake was extracted with boiling water. The combined filtrates were evaporated to dryness under reduced pressure and the residue recrystallized from ethanol to give 0.81 g. (79.5%) of pale brown prisms, m.p. 241–243°, identical with the product obtained by method (*a*) above.

2,4-Diamino-5-nitro-6-methylpyrimidine (IV). Method *a*. A suspension of 2 g. of 2-amino-4-benzyloxyamino-5-nitro-6-methylpyrimidine in 20 ml. of ethanol and 20 ml. of concentrated ammonium hydroxide was saturated with hydrogen sulfide and then heated under reflux for 30 min. Addition of 60 ml. of water followed by cooling caused the separation of a yellow solid which was collected by filtration and dissolved in dilute hydrochloric acid. Extraction of this acidic solution with methylene chloride removed a small amount of oily material. Neutralization of the aqueous layer with dilute ammonium hydroxide precipitated a yellow solid which was recrystallized from ethanol to give 0.9 g. (73%) of yellow needles, m.p. 235–236°. A mixture melting point determination with a sample of authentic 2,4-diamino-5-nitro-6-methylpyrimidine prepared as described below showed no depression. The reported melting point for a crude sample of this material is 235° dec.[7]

Method *b*. A solution of 2 g. of 2-amino-4-chloro-5-nitro-6-methylpyrimidine in 125 ml. of ethanol was saturated with dry ammonia and then heated under reflux for 2 hr. while ammonia was passed continually through the refluxing solution. The reaction mixture was cooled overnight and filtered to give 1.4 g. of crude product, m.p. 237–240°. A further quantity (0.2 g.) was obtained by concentration of the filtrate. Recrystallization of the combined crude products from ethanol yielded 1.45 g. (80.5%) of yellow needles, m.p. 235–236°.

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Effect of Molecular Size and Structure on the Pyrolysis of Esters. II[1]

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It has been demonstrated that a change in the size of the acyl portion of esters causes a change in the ease of their pyrolysis.[1] For example, esters of stearic acid pyrolyze at a lower temperature than esters of acetic or formic acid. The decrease, however, in the temperature of pyrolysis as the acyl portion increases in size by one methylene group is not a regular decrease; rather it decreases in a zigzag fashion with esters from acids of an even number of carbon atoms being slightly more stable than their neighboring homologues.

The question as to whether this effect is due to a change in the size of the acyl portion or a change in the molecular weight of the ester was not answered.

Nine isomeric normal aliphatic primary esters of molecular weight 200 and formula $C_nH_{2n+1}CO_2C_mH_{2m+1}$ ($n + m = 12$) have been pyrolyzed under conditions identical to those reported in the earlier study. The results from this study clearly demonstrate that the ease of pyrolysis of esters is a function of molecular weight (or size) of the ester and not of the acyl portion alone.

In comparing the ease of pyrolysis of the nine esters their "characteristic temperatures"[2] were determined by passing a constant amount at a definite rate through a flow system and measuring the extent of pyrolysis at seven different temperatures over a range of 81°. The extent of pyrolysis in this temperature range was from 6.9 to 96.3 per cent. All esters studied showed a characteristic

TABLE I

PYROLYSIS OF ALKANOATES OF THE FORMULA $C_nH_{2n+1}CO_2C_mH_{2m+1}$

Name	Yield, %	B.p.		n_D	d_{20}^{20}	Analysis				Characteristic Temp., °C.	Yield, % at C.T.
						Carbon, %		Hydrogen, %			
		°C.	Mm.			Calcd.	Found	Calcd.	Found		
Ethyl decanoate	83	114–116[a]	20	1.4257[b,c]	0.8708[b,d]					561	
Propyl nonoate	82	127–129[e]	21	1.4236[f,g]	0.8637[h]					562	94.7
Butyl octanoate	93	122–125[i]	20	1.4229[f,j]	0.8646					558	95.5
Pentyl heptanoate	87	120–126[k]	20	1.4233[f,l]	0.8632					562	92.0
Hexyl hexanoate	93	125–126	20	1.4249[b]	0.8630[m]	71.95	71.79	12.08	11.79	561	93.0
Heptyl pentanoate	91	124–126	20	1.4248[b]	0.8610[n]	71.95	72.08	12.08	11.87	560	92.4
Octyl butanoate	75	120–123	19	1.4250[b]	0.8621[o]	71.95	72.00	12.08	11.96	560	91.3
Nonyl propanoate	85	126–128	20	1.4259[b]	0.8637	71.95	72.02	12.08	11.91	559	94.8
Decyl acetate	88	126–127[p]	20	1.4272[b,q]	0.8654[r]					561	96.3

[a] Reported[3] b.p. 122–124°/13 mm. [b] 20°. [c] Reported[4] n_D^{45} 1.4154. [d] Reported[5] d_4^{20} 0.862. The low yield (14.4%) in the pyrolysis of this ester was demonstrated to be caused by contamination of the ethyl decanoate with methyl decanoate by conversion to the 3,5-dinitrobenzoate, m.p. 107–108°. The methyl ester is stable to pyrolysis at this temperature. [e] Reported[6] b.p. 120–122°/20 mm. [f] 25°. [g] Reported[6] n_D^{25} 1.4236. [h] Reported[6] d_4^{25} 0.8540. [i] Reported[6] b.p. 121–122°/20 mm. [j] Reported[6] n_D^{25} 1.4232. [k] Reported[6] b.p. 118–119°/20 mm. [l] Reported[6] n_D^{25} 1.4231. [m] Reported[7] d^{30} 0.85414. [n] Reported[7] d_4^{15} 0.86625. [o] Reported[7] d_4^{15} 0.86686. [p] Reported[8] b.p. 125–126°/15 mm. [q] Reported[9] n_D^{20} 1.4272. [r] Reported[10] d_4^{20} 0.8671.

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[1] Previous paper in this series, *J. Am. Chem. Soc.*, **79**, 875 (1957).

[2] The "characteristic temperature" has been defined[1] as the temperature at which a maximum is obtained from a plot of percentage yield divided by pyrolysis temperature *vs.* the pyrolysis temperature. In effect the characteristic temperature is that temperature at which the most efficient pyrolysis takes place when the rate of flow is constant.