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Syntheses of 1,6-Dimethylpyrimido[4,5-*c*]pyridazine-5,7(1*H*, 6*H*)-diones (4-Deazatoxoflavins) and Their Use in the Autorecycling Oxidation of Alcohols and Amines

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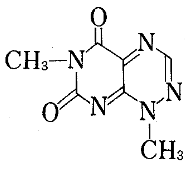
Treatment of 3-methyl-6-(1-methylhydrazino)uracil (I) with phenacyl bromides in ethanol afforded the corresponding 3-aryl-4,8-dihydro-1,6-dimethylpyrimido[4,5-*c*]-pyridazine-5,7(1*H*,6*H*)-diones (3-aryl-4,8-dihydro-4-deazatoxoflavins) (II) and 3-aryl-1,7-dimethyl-6,8-dioxo-1,4,6,7,8-pentahydropyrimido[4,3-*c*]-*as*-triazines (III). Oxidation of II with diethyl azodicarboxylate gave the corresponding 3-aryl-4-deazatoxoflavins (IV) in quantitative yields. The reaction of aryl aldehyde N-methyl-N-(3-methyluracil-6-yl)-hydrazones (VII) with triethyl orthoformate in dimethylformamide also gave the corresponding 3-aryl-4-deazatoxoflavins (IV).

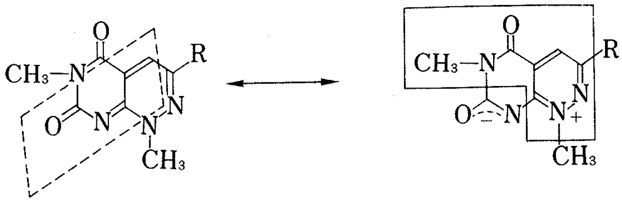
Compounds IV thus obtained oxidized alcohols under alkaline conditions in the dark to yield the corresponding carbonyl compounds, while they themselves were hydrogenated to compounds II. Under certain conditions, these oxidations were automatically recycled to give the corresponding carbonyl compounds in more than 100% yields.

Keywords——pyrimido[4,5-*c*]pyridazine; pyrimido[4,3-*c*]-*as*-triazine; 4-deazatoxoflavin; 4,8-dihydro-4-deazatoxoflavin; biomimetic oxidation of alcohol; biomimetic oxidation of amine; autorecycling; turn-over catalyst; NAD$^+$ model

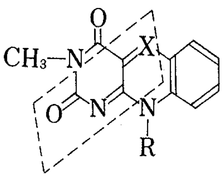
1,6-Dimethylpyrimido[4,5-*c*]pyridazine-5,7(1*H*,6*H*)-dione (4-deazatoxoflavin), in which N-4 of the antibiotic toxoflavin[1] is replaced by CH, has a conjugated system similar to that of flavin and 5-deazaflavin.[2,3] Furthermore, one of its canonical forms can be considered as a model of the 6-aza-analog of nicotinamide nucleotide. Therefore it would be expected that 4-deazatoxoflavin derivatives might abstract hydrogen equivalents from hydrogen donors under certain conditions. 4-Deazatoxoflavin and its analogs were first synthesized by Castle and coworkers[4] through condensation of 3-methyl-6-(1-methylhydrazino)uracil with appropriate α-diketones. This paper describes two new synthetic approaches to 4-deazatoxoflavin



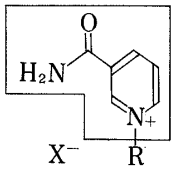
toxoflavin



4-deazatoxoflavin



X=N; flavin
X=CH; 5-deazaflavin



nicotinamide nucleotide

Chart 1

derivatives and their use as an autorecycling oxido-reductive catalyst in the oxidation of alcohols and amines.

Syntheses of 4-Deazatoxoflavins

One of our synthetic procedures (method A) for 4-deazatoxoflavins involves the condensation of 3-methyl-6-(1-methylhydrazino)uracil (I)⁵⁾ with the appropriate phenacyl bromides. For example, refluxing of I with an equimolar amount of phenacyl bromide in ethanol afforded a mixture of 4,8-dihydro-1,6-dimethyl-3-phenylpyrimido[4,5-*c*]pyridazine-5,7(1*H*,6*H*)-dione (4,8-dihydro-3-phenyl-4-deazatoxoflavin) (IIa) and 1,7-dimethyl-6,8-dioxo-3-phenyl-1,4,6,7,8-pentahydropyrimido[4,3-*c*]-*as*-triazine (IIIa). Prolonged heating of the above mixture gave 3-phenyl-4-deazatoxoflavin (IVa) (*vide infra*), besides IIa and IIIa. However, the best way to

TABLE I. 3-Aryl-4,8-dihydro-1,6-dimethylpyrimido[4,5-*c*]pyridazine-5,7(1*H*,6*H*)-diones (II) and 3-Aryl-1,7-dimethyl-6,8-dioxo-1,4,6,7,8-pentahydropyrimido[4,3-*c*]-*as*-triazines (III)

Compd. No.	R	Yield (%)	mp[a] (°C)	Appearance	Formula	Analysis (%) Calcd. (Found) C	H	N
IIa	C_6H_5	68	256	Pale yellow powder	$C_{14}H_{14}N_4O_2$	62.21 (62.34	5.22 5.20	20.73 20.39)
IIb	4-Br-C_6H_4	70	254	Pale yellow powder	$C_{14}H_{13}BrN_4O_2$	48.15 (47.90	3.75 3.46	16.03 16.28)
IIc	4-Cl–C_6H_4	75	253	Pale yellow powder	$C_{14}H_{13}ClN_4O_2$	55.18 (55.07	4.30 4.31	18.39 18.11)
IIIa	C_6H_5	10	235	Yellow needles	$C_{14}H_{14}N_4O_2$	62.21 (62.33	5.22 5.08	20.73 20.47)
IIIb	4-Br–C_6H_4	16	276	Yellow needles	$C_{14}H_{13}BrN_4O_2$	48.15 (48.25	3.75 3.74	16.03 16.24)
IIIc	4-Cl–C_6H_4	10	286	Yellow needles	$C_{14}H_{13}ClN_4O_2$	55.18 (54.89	4.30 4.22	18.39 18.42)

[a] All compounds were recrystallized from ethanol.

TABLE II. 3-Aryl-1,6-dimethylpyrimido[4,5-*c*]pyridazine-5,7(1*H*,6*H*)-diones (3-Aryl-4-deazatoxoflavins) (IV)

Compd. No.	R	Yield by Method B (%)	mp[a] (°C)	Formula	Analysis (%) Calcd. (Found) C	H	N
IVa	C_6H_5	35	250	$C_{14}H_{12}N_4O_2$	62.68 (62.57	4.51 4.55	20.89 20.77)
IVb	4-Br–C_6H_4	29	256	$C_{14}H_{11}BrN_4O_2$	48.43 (48.25	3.19 3.17	16.14 16.01)
IVc	4-Cl–C_6H_4	30	248	$C_{14}H_{11}ClN_4O_2$	55.54 (55.38	3.66 3.41	18.51 18.76)
IVd	4-F–C_6H_4	45	258	$C_{14}H_{11}FN_4O_2$	58.74 (58.54	3.87 3.89	19.57 19.64)
IVe	3,4-Cl_2–C_6H_3	35	240	$C_{14}H_{10}Cl_2N_4O_2$	49.87 (49.64	2.99 3.07	16.62 16.63)
IVf	2,4-Cl_2–C_6H_3	30	254	$C_{14}H_{10}Cl_2N_4O_2$	49.87 (49.92	2.99 3.03	16.62 16.79)
IVg	3,4-CH_2O_2–C_6H_3	35	287	$C_{15}H_{12}N_4O_4$	57.69 (57.78	3.87 3.94	17.94 17.65)
IVh	3,4-$(CH_3O)_2$–C_6H_3	25	303	$C_{16}H_{16}N_4O_4$	58.53 (58.42	4.91 4.73	17.07 16.95)

[a] All compounds were recrystallized from ethanol as yellow needles.

get IVa was the diethyl azodicarboxylate (DAD) oxidation[6] of IIa initially formed. Thus, the stirring of IIa with excess DAD at 90° for just a few minutes afforded 3-phenyl-4-deazatoxoflavin (IVa) in quantitative yield. Other 4,8-dihydro-4-deazatoxoflavins (IIb, c) and pyrimido[4,3-*c*]-*as*-triazine derivatives (IIIb, c) were similarly prepared by refluxing I with the corresponding phenacyl bromides in ethanol (Table I). Compounds IIb, c were converted into the corresponding 4-deazatoxoflavins (IVb, c) by treatment with DAD. Conversely, treatment of IV with sodium dithionite in aqueous ammonia afforded II as expected.

A remarkable solvent effect was noted during the reactions between I and phenacyl bromides; refluxing of the above mixture in dimethylformamide led to the exclusive formation of the corresponding pyrimido[4,3-*c*]-*as*-triazine derivatives (III). Furthermore, refluxing of the mixture in acetic acid gave a mixture of II, III, IV and 3,7-dimethyl-2,4,6,8-tetraoxo-1,2,3,4,6,7,8,9-octahydropyrido[2,3-*d*: 6,5-*d'*]dipyrimidine (V). The latter compound was identified by conversion into the known 1,3,7,9-tetramethyl derivative (VI)[7] by the conventional methylation with methyl iodide. The structures of compounds II, III and IV were derived on the basis of elemental analyses, molecular weights as determined by mass spectrometry, and nuclearmagnetic resonance (NMR) data (Table III).

Our second procedure (method B) consists of the intramolecular cyclization of the aryl aldehyde N-methyl-N-(3-methyluracil-6-yl)hydrazones (VII)[2] with triethyl orthoformate. For example, heating of benzaldehyde N-methyl-N-(3-methyluracil-6-yl)hydrazone (VIIa) with excess triethyl orthoformate in dimethylformamide gave IVa (identical with the sample prepared by Method A). Other 4-deazatoxoflavins (IV) were similarly synthesized (Table II). It should be noted that other one-carbon reagents such as dimethylformamide dimethylacetal or the Vilsmeier–type reagents were not effective for the above cyclization.

Oxidation of Alcohols and Amines by 4-Deazatoxoflavins

Previously we have found that 5-deazaflavins can oxidize alcohols under alkaline conditions even in the dark to yield the corresponding carbonyl compounds, while they themselves are hydrogenated to 1,5-dihydro-5-deazaflavins.[8] As was expected from their structure (similar to that of 5-deazaflavins), 4-deazatoxoflavins (IV) showed oxidizing ability toward

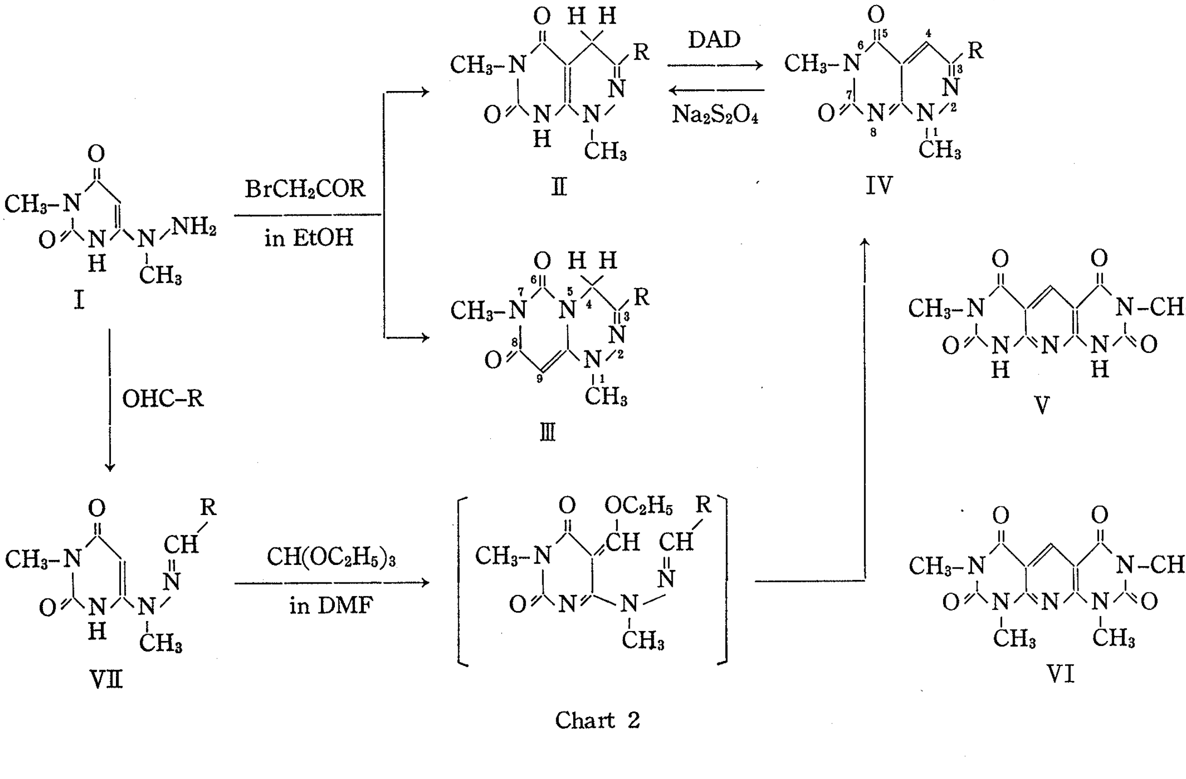


Chart 2

TABLE III. NMR Data for 4,8-Dihydro-4-deazatoxoflavins (II), Pyrimido-[4,3-*c*]-*as*-triazines (III) and 4-Deazatoxoflavins (IV)

Compd. No.	δ (CF_3COOH) ppm
IIa	3.54 (3H, s, N_6–CH_3), 3.75 (3H, s, N_1–CH_3), 3.93 (2H, s, C_4–H_2), 7.30—7.99 (5H, ArH)
IIb	3.55 (3H, s, N_6–CH_3), 3.71 (3H, s, N_1–CH_3), 3.78 (2H, s, C_4–H_2), 7.62 (4H, ArH)
IIc	3.54 (3H, s, N_6–CH_3), 3.71 (3H, s, N_1–CH_3), 3.78 (2H, s, C_4–H_2), 7.30—7.84 (4H, ArH)
IIIa	3.62 (3H, s, N_7–CH_3), 3.73 (3H, s, N_1–CH_3), 5.02 (2H, s, C_4–H_2), 5.80 (1H, s, br, C_9–H), 7.45—7.95 (5H, ArH)
IIIb	3.62 (3H, s, N_7–CH_3), 3.72 (3H, s, N_1–CH_3), 4.97 (2H, s, C_4–H_2), 5.82 (1H, s, br, C_9–H), 7.66 (4H, ArH)
IIIc	3.62 (3H, s, N_7–CH_3), 3.73 (3H, s, N_1–CH_3), 4.98 (2H, s, C_4–H_2), 5.82 (1H, s, br, C_9–H), 7.40—7.90 (4H, ArH)
IVa	3.64 (3H, s, N_6–CH_3), 4.74 (3H, s, N_1–CH_3), 7.55—8.25 (5H, ArH), 9.39 (1H, s, C_4–H)
IVb	3.65 (3H, s, N_6–CH_3), 4.75 (3H, s, N_1–CH_3), 7.68—8.12 (4H, ArH), 9.40 (1H, s, C_4–H)
IVc	3.63 (3H, s, N_6–CH_3), 4.71 (3H, s, N_1–CH_3), 7.51—8.17 (4H, ArH), 9.36 (1H, s, C_4–H)
IVd	3.63 (3H, s, N_6–CH_3), 4.77 (3H, s, N_1–CH_3), 7.50—8.30 (4H, ArH), 9.44 (1H, s, C_4–H)
IVe	3.65 (3H, s, N_6–CH_3), 4.76 (3H, s, N_1–CH_3), 7.60—8.30 (3H, ArH), 9.42 (1H, s, C_4–H)
IVf	3.66 (3H, s, N_6–CH_3), 4.76 (3H, s, N_1–CH_3), 7.60—7.80 (3H, ArH), 9.37 (1H, s, C_4–H)
IVg	3.62 (3H, s, N_6–CH_3), 4.66 (3H, s, N_1–CH_3), 6.07 (2H, s, –O–CH_2–O–), 6.92—7.78 (3H, ArH), 9.25 (1H, s, C_4–H)
IVh	3.65 (3H, s, N_6–CH_3), 4.08 (3H, s, OCH_3), 4.12 (3H, s, OCH_3), 4.73 (3H, s, N_1–CH_3), 7.12—7.98 (3H, ArH), 9.45 (1H, s, C_4–H)

alcohols in the presence of potassium hydroxide to yield the corresponding carbonyl compounds in stoichiometric yield.[9]

We have now found that 4-deazatoxoflavin-dependent oxidation of alcohols is automatically recycled under less basic conditions.[10] Stirring of a mixture of a 3-aryl-4--deazatoxoflavin (IV) and potassium carbonate in an appropriate alcohol under aerobic conditions at 90° gave the corresponding carbonyl compound, which was identified as the 2,4-dinitrophenylhydrazone. Under these conditions, the 4,8-dihydro-4-deazatoxoflavins (II) initially formed are reoxidized to the original 4-deazatoxoflavins (IV) by adventitious air and then IV acted as a turn-over catalyst (see Chart 3).

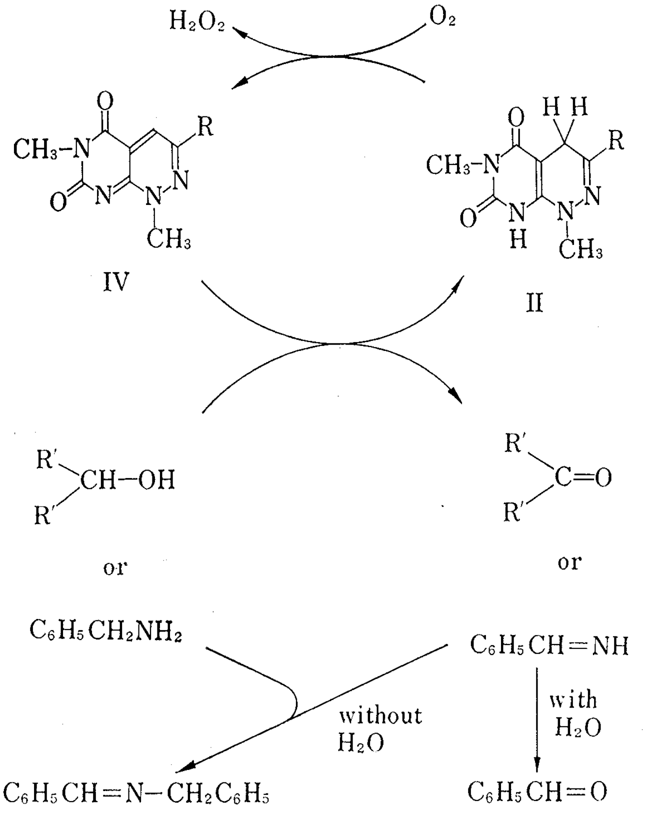


Chart 3

Table IV shows the experimental results of alcohol oxidations by several 4-deazatoxoflavins (IV). In this series, a significant substituent effect was observed; in particular, 3-(4-fluorophenyl)-4-deazatoxoflavin (IVd) exhibited a strong oxidizing ability toward both benzyl alcohol and cyclohexanol.

It should be noted here that 3-(2,4-dichlorophenyl)-4-deazatoxoflavin (IVf) did not oxidize alcohols to any appreciable degree. This is presumably attributable to the non-planarity of this compound on account of the *o*-

chloro-group and to hindrance to the formation of a complex between the 4-deazatoxoflavin and alcohols.

Next, the oxidation of benzylamine by IV was carried out under aqueous and nonaqueous conditions. Heating IV in 50% aqueous benzylamine at 90° under stirring gave benzaldehyde, which was also identified as the 2,4-dinitrophenylhydrazone (Table V). This is a biomimetic

TABLE IV. Oxidation of Benzyl Alcohol and Cyclohexanol by 3-Aryl-4-deazatoxoflavins (IV) at 90°

Compd. No.	R	Yield[a] (Yield)[b] (%)	
		Benzaldehyde[c] (after 5 hr)	Cyclohexanone[c] (after 10 hr)
IVa	C_6H_5	191 (7)	135 (5)
IVb	4-Br–C_6H_4	325 (12)	370 (14)
IVc	4-Cl–C_6H_4	365 (14)	253 (9)
IVd	4-F–C_6H_4	660 (25)	618 (23)
IVe	3,4-Cl_2–C_6H_3	239 (9)	244 (9)
IVf	2,4-Cl_2–C_6H_3	65 (2)	60 (2)
IVg	3,4-CH_2O_2–C_6H_3	<100 (<4)	<100 (<4)
IVh	3,4-$(CH_3)_2$–C_6H_3	<100 (<4)	<100 (<4)

a) Based on the 4-deazatoxoflavins.
b) Based on the starting alcohols in parentheses.
c) Isolated as 2,4-dinitrophenylhydrazone.

TABLE V. Oxidation of Benzylamine to Benzaldehyde by 4-Deazatoxoflavins (IV) under Aqueous Conditions at 90°

Compd. No.	R	Yield[a] (Yield)[b] (%) Benzaldehyde[c] (after 10 hr)
IVa	C_6H_5	160 (6)
IVb	4-Br–C_6H_4	331 (12)
IVc	4-Cl–C_6H_4	355 (13)
IVd	4-F–C_6H_4	419 (17)

a) Yield based on the 4-deazatoxoflavins.
b) Yield based on the benzylamine is given in parentheses.
c) Isolated as the 2,4-dinitrophenylhydrazone.

TABLE VI. Oxidation of Benzylamine to Benzaldehyde by 4-Deazatoxoflavins (IV) under Nonaqueous Conditions at 90°

Compd. No.		Yield[a] (Yield)[b] (%) Benzaldehyde[c]		
		(after 10 hr)	(after 20 hr)	(after 40 hr)
IVa	C_6H_5	2013 (15)	4682 (35)	
IVb	4-Br–C_6H_4	3561 (27)	6257 (47)	
IVc	4-Cl–C_6H_4	3000 (22)	5352 (40)	10579 (79)
IVd	4-F–C_6H_4	7340 (27)[d]	14254 (53)[d]	25370 (95)[d]
IVg	3,4-CH_2O_2–C_6H_3	1808 (13)	4189 (31)	
IVh	3,4-$(CH_3O)_2$–C_6H_3	470 (4)	960 (7)	

a) Yield based on the 4-deazatoxoflavins.
b) Yield based on the benzylamine is given in parentheses.
c) Isolated as the 2,4-dinitrophenylhydrazone.
d) Reaction between IVd (0.000175 mol) and benzylamine (10 ml).

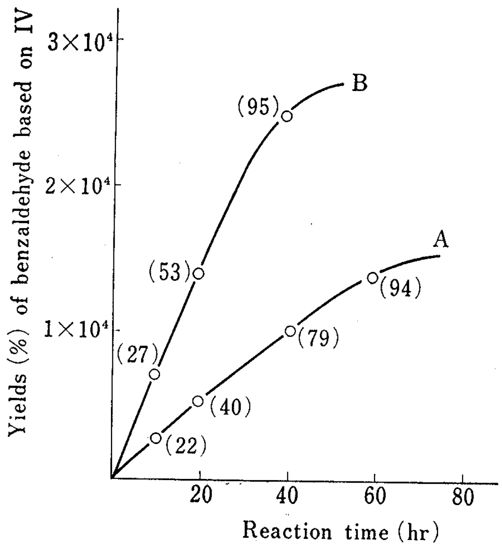


Fig. 1. Oxidation of Benzylamine by 4-Deazatoxoflavins under Nonaqueous Conditions at 90°

A; Reaction between IVc (0.00035 mol) and benzylamine (10 ml). B; Reaction between IVd (0.000175 mol) and benzylamine (10 ml). The numbers in parentheses show the yields based on the starting benzylamine.

conversion of an amine to a carbonyl compound *via* the imine by an NAD^+ model.

When the reaction between IV and benzylamine was carried out in the absence of water, a remarkable recycling of its oxidation into benzylideneamine was observed. The latter was readily condensed with excess benzylamine, with evolution of ammonia to give rise to benzylidenebenzylamine, which accumulated in the reaction mixture. The benzylidenebenzylamine was also treated with 2,4-dinitrophenylhydrazine to give benzaldehyde 2,4-dinitrophenylhydrazone in the yields indicated in Table VI and Fig. 1. This oxidation proceeded very efficiently until the benzylamine was almost exhausted, as can be seen from Fig. 1.

In control experiments without IV in the above alcohol and amine oxidations, at most only a trace of carbonyl compounds was detected. We consider that such an autorecycling oxidation of alcohols and amines is interesting from a resource-economizing as well as an organic chemical point of view.

Experimental[11]

Reaction of 3-Methyl-6-(1-methylhydrazino)uracil (I) with Phenacyl Bromides. Procedure A——A phenacyl bromide (0.012 mol) was added to a solution of I (2 g, 0.012 mol) in ethanol (40 ml), and the mixture was refluxed for 1.5 hr. While the reaction mixture was warm, crystals which had separated were filtered off, washed with ethanol and dried to give a 4,8-dihydro-4-deazatoxoflavin (II). The filtrate was evaporated to dryness *in vacuo* to give a crude pyrimido[4,3-*c*]-*as*-triazine (III) (see Table I).

Procedure B——A phenacyl bromide (0.012 mol) was added to a solution of I (2 g, 0.012 mol) in dimethylformamide (30 ml), and the mixture was refluxed for 1.5 hr. The reaction mixture was evaporated to dryness *in vacuo* and the residue was treated with ethanol to separate the corresponding pyrimido[4,3-*c*]-*as*-triazine (III) exclusively. Yield: IIIa 73%; IIIb 80%; IIIc 78%.

Procedure C——A phenyl bromide (0.012 mol) was added to a solution of I (2 g, 0.012 mol) in acetic acid (40 ml), and the mixture was refluxed for 5 hr. After cooling, the separated crystals were filtered off, and washed with ethanol to give the corresponding 4,8-dihydro-4-deazatoxoflavin (II) in 6—10% yield. The filtrate was concentrated *in vacuo* and the residue was recrystallized from ethanol to give the corresponding 4-deazatoxoflavin (IV) in 48—50% yield. The filtrate from the above recrystallization was evaporated to dryness and the residue was recrystallized fractionally from ethanol to give a pyrimido[4,3-*c*]-*as*-triazine (III) and 3,7-dimethyl-2,4,6,8-tetraoxo-1,2,3,4,6,7,8,9-octahydropyrido[2,3-d: 6,5-d′]dipyrimidine (V) in 20—30 and 5—8% yields, respectively. Compound V had mp>360° (from dimethylformamide). MS *m/e*: 275 (M^+). *Anal.* Calcd for $C_{11}H_9N_5O_4$: C, 48.00; H, 3.30; N, 25.45. Found: C, 48.21; H, 3.31; N, 25.39.

4-Deazatoxoflavins (IV) Formation by the Oxidation of 4,8-Dihydro-4-deazatoxoflavins (II) with DAD. General Procedure——Compound II (0.0035 mol) was treated with excess DAD (0.007—0.01 mol) and the mixture was heated at 90° for 5—10 min under stirring. After cooling, the reaction mixture was diluted with ether and crystals which separated were filtered off. Recrystallization from a mixture of ethanol and dimethylformamide gave the corresponding IV in quantitative yield.

Synthesis of 4-Deazatoxoflavins (IV) by the Condensation of Aryl Aldehyde N-Methyl-N-(3-methyluracil-6-yl)hydrazones (VII) with Triethyl Orthoformate. General Procedure——A mixture of an aryl aldehyde N-methyl-N-(3-methyluracil-6-yl)hydrazone (VII) (0.0037 mol) and triethyl orthoformate (0.03 mol) in dimethylformamide (5 ml) was gently refluxed for 10 hr. The reaction mixture was evaporated to dryness and the residue was treated with a small amount of ethanol to separate crystals, which were filtered off and dried. Recrystallization from ethanol gave IV in the yields indicated in Table II.

Reduction of 4-Deazatoxoflavins (IV) with Sodium Dithionite. General Procedure——One of the compounds IV (0.0037 mol) and sodium dithionite (0.012 mol) were added to 10% aqueous ammonia (10 ml), and the mixture was heated at 90° for 1 hr with stirring. The mixture was cooled, then the resulting crystals were filtered off, dried and recrystallized from acetic acid to give the corresponding II in 60—65% yield.

Oxidation of Alcohols by 4-Deazatoxoflavins (IV). General Procedure——A mixture of IV (0.00035 mol) and potassium carbonate (0.001 mol) in benzyl alcohol or cyclohexanol (1 ml) was stirred at 90° under aerobic conditions. The reaction mixture was diluted with ether and the crystals (including recovered IV and its reduced compound II) thus obtained were filtered off. The filtrate was treated with a 2 N hydrochloric acid solution of 2,4-dinitrophenylhydrazine to give the corresponding 2,4-dinitrophenylhydrazone of benzaldehyde or cyclohexanone (see Table IV).

Oxidation of Benzylamine by 4-Deazatoxoflavins (IV) under Aqueous Conditions. General Procedure——Heating a solution of IV (0.00035 mol) in 50% aqueous benzylamine (2 ml) under stirring, followed by the procedure described above, gave benzaldehyde 2,4-dinitrophenylhydrazone (see Table V).

Oxidation of Benzylamine by 4-Deazatoxoflavins (IV) under Nonaqueous Conditions. General Procedure——A mixture of IV (0.00035 mol) and benzylamine (10 ml) was heated at 90°. The reaction mixture, which includes benzylidenebenzylamine, was treated with a 2 N hydrochloric acid solution of 2,4-dinitrophenylhydrazine to give benzaldehyde 2,4-dinitrophenylhydrazone in the yields indicated in Table VI.

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