Nach dieser Methode wurden *4-Amino-3-jod-benzonitril* und *2-Jod-4-nitro-anilin* in einer Ausbeute von 95–97% der Theorie erhalten.

Smp. wie Elementaranalyse der jodierten Derivate stimmten mit den Literaturangaben bzw. den berechneten Werten überein.

2-Brom-6-Jod-4-nitro-anilin. Diese noch nicht beschriebene Substanz erhielt man nach diesem Verfahren, nach Umkristallisation aus Toluol und Aceton, in gelben, nadelförmigen Kristallen (Smp., korr.: 234–235°) in 88% Ausbeute. NMR.-Spektren bestätigten die Konstitution.

$C_6H_4BrJN_2O_2$	Ber. C 21,0	H 1,17	J 37,0	N 8,16%
	Gef. ,, 21,8	,, 1,2	,, 35,1	,, 8,3 %

LITERATURVERZEICHNIS

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157. The Synthesis and Borohydride Reduction of some Alloxazine Derivatives

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(15. III. 71)

Summary. Unequivocal syntheses of N(1 or 3)-mono-substituted 7,8-dimethylalloxazines are described. The borohydride reduction of various alloxazines has been studied under aerobic and anaerobic conditions, in the absence of light. These reactions are discussed in relation to other work on 7,8-dimethylisoalloxazines (flavins) and on certain flavoproteins.

Unambiguous syntheses for mono-N-methyl-7,8-dimethyl-alloxazines and their physical properties have been described, together with the behaviour of these and related derivatives towards lithium borohydride. The deprotonation and chemical reactions of 7,8-dimethylalloxazines have been studied in connection with related studies of some model 7,8-dimethyl-isoalloxazines (flavins) and of certain flavoproteins [1–5].

None of the methods available for the synthesis of 7,8-dimethyl-alloxazine derivatives, namely: (1) condensation of the appropriate diamine with alloxan [6], (2)

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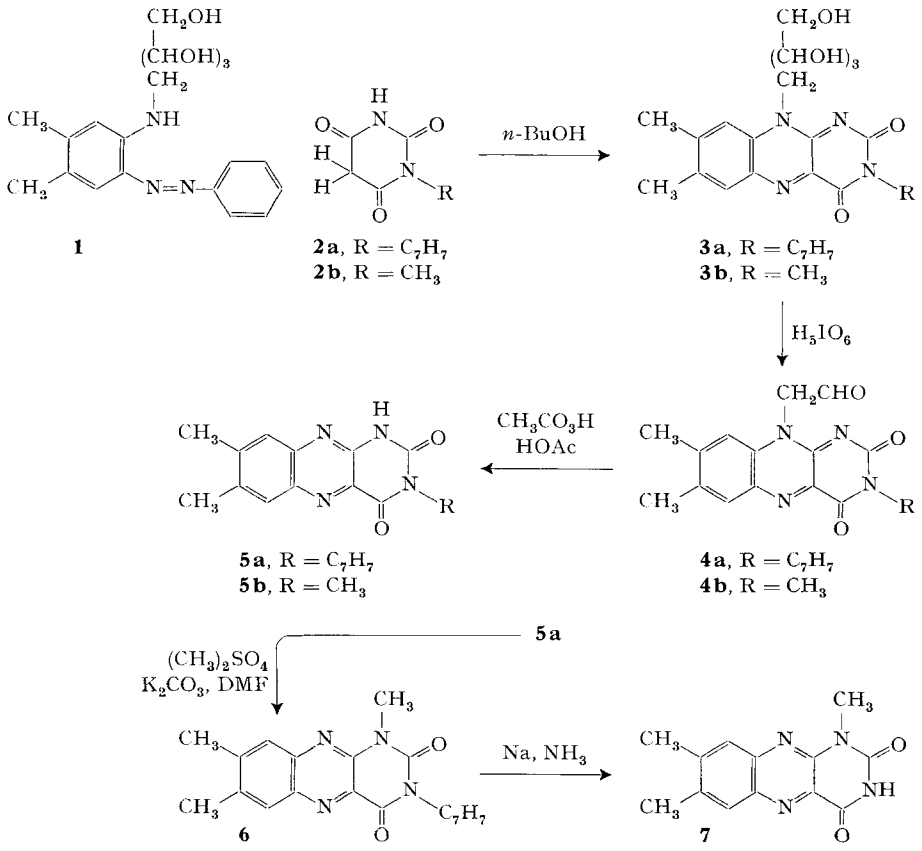
photolysis of a riboflavin analogue in a neutral medium [7], or (3) hydroxylamine-induced N(10)-methyl dealkylation of a lumiflavin in acetic acid solution [8], is suitable for the unambiguous synthesis of an N(3)- or N(1)-mono-alkyl-alloxazine. The use of method (1) in this particular case would be impractical because of the uncertainty involved with regard to the positions of attachment of the so formed pyrazine ring. The low water solubility of N(3)-alkylated riboflavins renders the photolysis procedure (2) inconvenient. Compared to the known example of lumiflavin [8], hydroxylamine-induced N(10)-dealkylation of N(3)-alkylated lumiflavins is more complex, depending on the N(3)-substituent [9]. We sought, therefore, an unequivocal synthesis of N(1)- and N(3)-monoalkylated alloxazine derivatives.

Results. – The primary intermediate utilized for synthesis of 1,7,8-trimethyl-alloxazine (**7**) was N(3)-benzylriboflavin (**3a**), obtainable in adequate yield (~50%) using the barbituric acid condensation method of *Tishler et al.* [10] [11] (Scheme I).

The riboflavin **3a** was converted by periodic acid [12], in acetic acid solution, to the 10-formylmethyl-flavin **4a**, which, by heating under reflux with peroxyacetic acid, underwent facile oxidative transformation at N(10) to yield N(3)-benzyl-7,8-dimethyl-alloxazine (**5a**). In successive steps, **5a** was methylated by dimethylsulfate

Scheme I

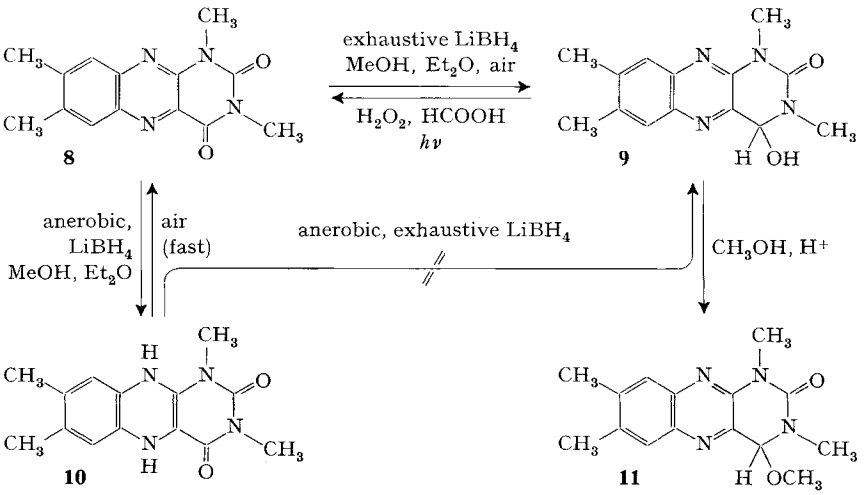


in N,N-dimethylformamide-potassium carbonate mixture [13], to give **6** which was N(3)-debenzylated by sodium in ammonia so affording the desired 1,7,8-trimethylalloxazine (**7**). An attempt to remove the N(3)-benzyl group of **6** by catalytic hydrogenation (H_2/Pd–C) failed. In this context, it is noteworthy that N(3)-benzyllumiflavin could not be debenzylated by either procedure [9].

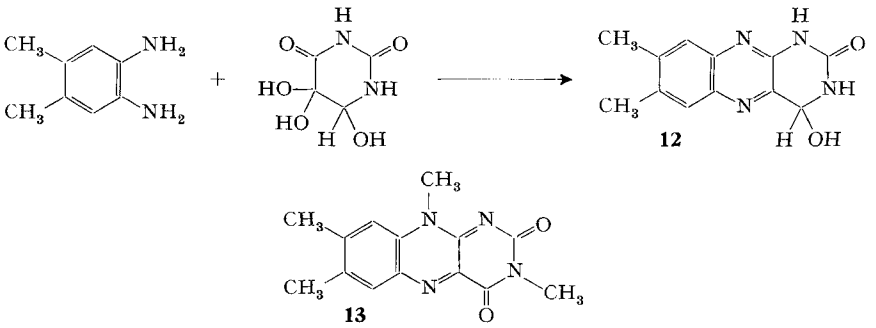
The synthesis of 3,7,8-trimethylalloxazine (**5b**) was accomplished similarly, the requisite riboflavin intermediate **3b** having been obtained according to *Föry & Hemmerich* [10]. *Fall & Petering's* periodic acid procedure [12] applicable for conversion of **3b** to **4b**, and the latter was heated under reflux with peroxyacetic acid solution to form **5b**.

The spectrophotometric ionization exponents, pK_a ($\mu = 0.1$, 25°), of **7** and **5b** were 8.65 ± 0.05 and 8.50 ± 0.05, respectively. The acidities of these compounds and the spectral changes that occurred by variation of pH in aqueous solutions paralleled properties of the closely related mono-N-methylpteridine-2(1*H*),4(3*H*)-diones [14]. In addition it was evident, from the light absorption data of **7** and **5b** at pH 13, that the N(3*H*) analogue **7** was exceptionally stable (no change in spectral properties after

Scheme II



Scheme III



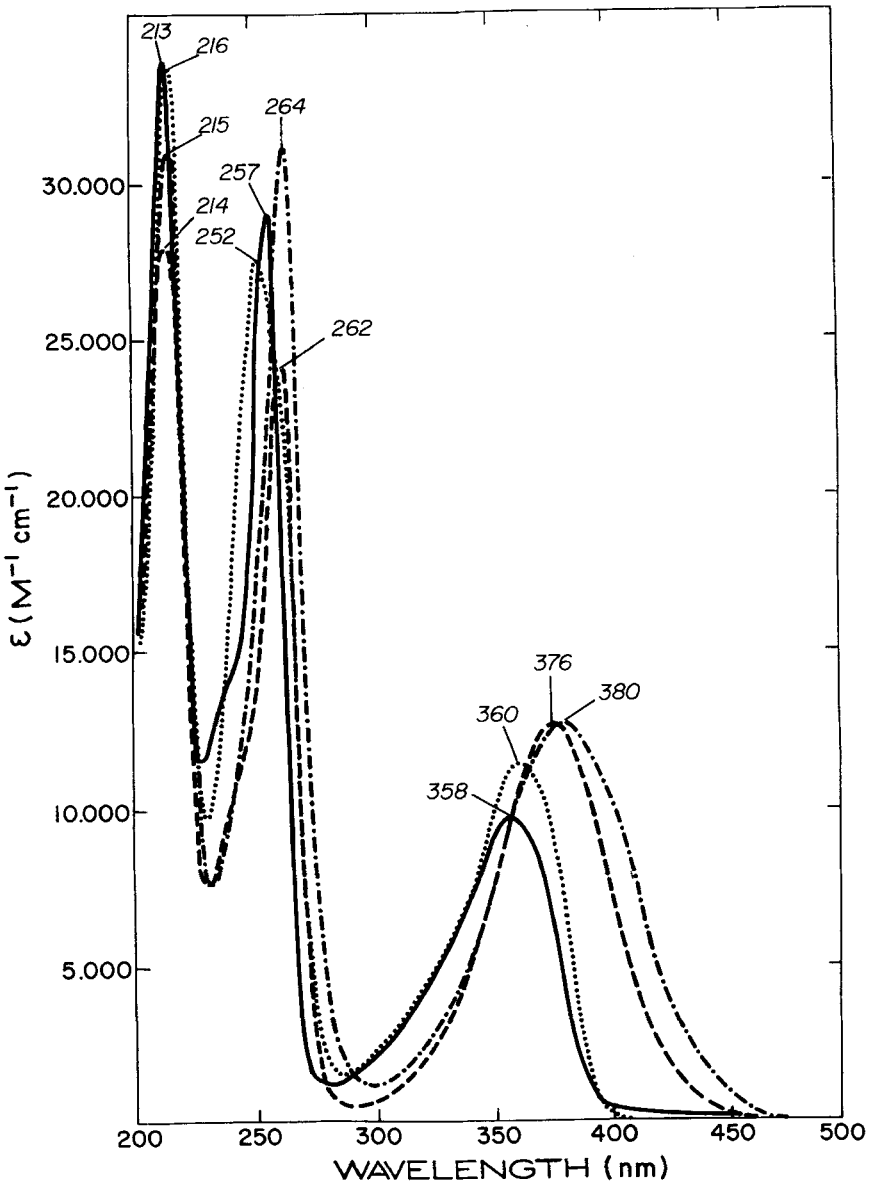


Figure 1. *Light absorption spectra of neutral and cationic species of compounds* **9** *and* **12**, *respectively*
In 0.1 M phosphate buffer, pH 6.5: ····· **9**, —— **12**; in 5 N HCl: ·–·–· **9**, – – – **12**

several days) at high pH, whereas the N(1*H*) analogue **5b** underwent decomposition, presumably to 2-methylamino-6,7-dimethyl-quinoxaline-3-N-methylcarboxamide. This conclusion was based upon the absorption maxima and spectral properties of **5b** and was in agreement with the findings of *Bredereck* & *Pfleiderer* [15] and of *Koziol* [16]. In the present study it was observed, as expected, that alloxazines such as

6 and **8**, underwent similar hydrolytic reactions at high pH, except that the reaction was more rapid.

The mono-N-alkylated 7,8-dimethylalloxazines, **5b** and **7**, did not react with lithium borohydride under the conditions previously described for the free isoalloxazines [1]. We found, however, that treatment of N(1),N(3),7,8-tetramethylalloxazine (**8**) by borohydride in air induces reduction of O=C(4) to form **9** (Scheme II). When this reaction was conducted under anaerobic conditions, the air-sensitive 1,5-dihydro derivative **10** was formed, as indicated by the UV. spectral properties of its solutions under anaerobic and aerobic conditions [4] [5].

The structure of the 'imidol' derivative **9** was supported by lack of the characteristic IR. absorption attributable to the 4-oxo group ($\sim$1720 cm^{-1}) of the alloxazine-2,4-diones. The presence of $>$CHOH was substantiated by the NMR.-spectrum showing the presence of an *AB* quartet [centers at δ6.87 ($>$CHO*H*) and δ5.77 ($>$C*H*OH)]; deuterium exchange reduced this *AB* system to an one-proton singlet (δ5.77, $>$CHOD). Further support of the 'imidol' structure was obtained by preparation of its O-methyl derivative **11**, formed smoothly on addition of a trace of mineral acid to a methanolic solution of **9**.

Compelling evidence for the positions of hydrogen addition to **8** was furnished by the unequivocal synthesis of the analogue **12** (see Scheme III).

The UV. and visible spectra of **12** were similar to those of the reduction product **9**; the absorption spectra of neutral and cationic forms of **9** and **12**, respectively, are shown in Fig. 1.

Attempts to convert **12** to **9** by direct alkylation, by means of (a) CH_3I, dimethylformamide, K_2CO_3 or (b) CH_3I, acetone, K_2CO_3, were unsuccessful, due apparently to the sensitivity of **12** towards bases.

9 is quantitatively reconverted (activated by light) to **8** by H_2O_2 in HCOOH; the accompanying spectral changes for this reaction are shown in fig. 2, isosbestic points at 384, 358 and 277 nm, respectively.

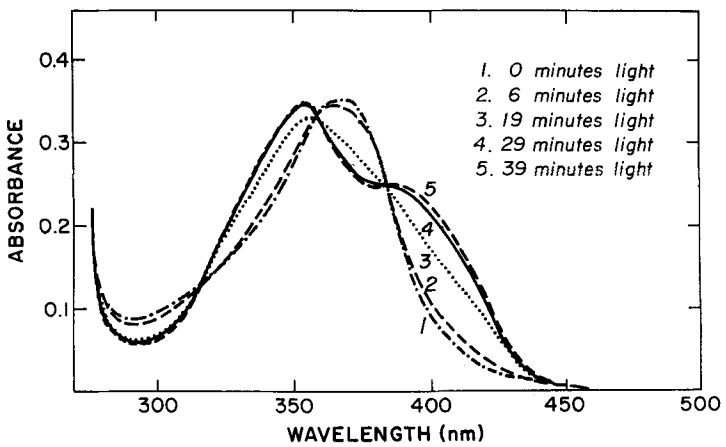


Figure 2. *Spectral change accompanying reconversion of* **9** *to* **8**

3.3×10^{-5} M with 3.5×10^{-1} M H_2O_2 in 20% aqueous HCOOH, illuminated by 100-W tungsten light bulb at room temperature for the time indicated

Fluorescence data of some of the compounds studied are summarized in Table I. For all compounds the fluorescence intensity value in pure water was higher than that in pure methanol. Those of the reduced alloxazines, **9** and **12**, are 4.5 times larger than those of the corresponding oxo compounds, **8** and 7,8-dimethylalloxazine (**14**), respectively. These trends are parallel to those with borohydride reduction products of flavins [1].

Discussion. – The borohydride reduction of an 'imide' function to an 'imidol' *i.e.*, –CONHCO– to –CONHCHOH–, has now been deduced from the nature of the final products or demonstrated in a number of cases, including hydantoins [4] [17], barbiturates [18], isoalloxazines (flavins) [1], and certain flavoproteins (D- and L-amino-acid oxidases) [3], which seem to be closely related to the alloxazines now studied. By a comparison of the alloxazines and isoalloxazines (including also the flavoprotein D-

Table 1. *Wavelength emission maximum on excitation, and fluorescence intensity of some 7,8-dimethyl-alloxazines*

Concentration $4 \cdot 10^{-5}$ M; the fluorescence intensity values are relative to **9** in H_2O (100%)

Compound	Solvent	Excitation wavelength in nm	Emission maximum in nm	Relative fluorescence intensity
	methanol	390	455	20.5
5a	H_2O	360	472	25.4
	0.1 N NaOH	435	528	59.8
	methanol	390	455	19.2
5b	H_2O	360	475	24.5
	0.1 N NaOH	435	527	58.2
	methanol	390	455	18.5
8	H_2O	365	472	20.2
	0.1 N NaOH	360	472	3.2[a]
	methanol	390	455	22.6
7	H_2O	360	473	25.8
	0.1 N NaOH	400	458	31.2
	methanol	365	412	80.5
9	H_2O	370	422	100.0
	0.1 N NaOH	365	412	2.4
	methanol	360	412	73.8
12	H_2O	365	420	94.0
	0.1 N NaOH	385	472	24.6
14	H_2O	360	472	26.2
	0.1 N NaOH	435	525	21.7

[a] Compound **8** is rather quickly hydrolyzed under these conditions; the low fluorescence intensity observed is that of the hydrolysate.

and L-amino-acid oxidases), pronounced differences are apparent in their susceptibility to borohydride. The alloxazines and isoalloxazines both yield a 1,5-dihydroflavin, **10**, by anaerobic borohydride reduction; this occurs in the absence or presence of light. Unless appropriately substituted at N(1) in order to block autoxidation [13], dihydroflavins of type **10** are extremely sensitive to air (in absence or presence of light) and

may be recognized not only by typical UV. spectra but also by their propensity for quantitative reoxidation to the oxo compound (**8** or **13**) on exposure to molecular oxygen [1].

Aerobic borohydride reduction of **8** to form **9** proceeded smoothly in the dark, whereas the reduction of the isoalloxazine **13** to a 3,4-dihydroflavin required photo-activation [1]. Unlike 1,5-dihydroflavins, *e.g.*, **10**, these reduction products are stable towards molecular oxygen in the dark, but they may be reconverted quantitatively to compounds of type **8** by hydrogen peroxide in formic acid solution, a reaction also photo-activated. That these reductions involve direct conversion of the 'oxidized form', *i.e.*, **8** and **13**, to their respective 'imidols' and do not proceed *via* the intermediate 1,5-dihydroflavins is consistent with the observation that 1,5-dihydroflavins produced from isoalloxazines and alloxazines are not further reduced by borohydride.

Where the flavin is the prosthetic group of an enzyme (D- and L-amino-acid oxidase), a modified coenzyme which contains a 3,4-dihydroflavin group (whilst retaining full catalytic activity) is formed upon reduction with borohydride without apparent restriction to the presence or absence of substrate, light, or molecular oxygen [2] [3]. This behaviour of the biological flavins parallels the borohydride susceptibility of the alloxazines here studied rather than that of the free isoalloxazines [1].

Experimental

M.p.'s were determined with a heating block (capillary) and are uncorrected. Infrared (IR.) spectra were recorded with a *Perkin-Elmer* 234 spectrophotometer; samples were prepared in the form of KBr discs consisting of 100 mg KBr and 0.3–0.4 mg of product. The numbers given in parentheses with the IR. and NMR. spectra indicate the position of the functional group.

Fluorescence spectra were measured with the ratio recording fluorimeter previously described [19]. Light absorption spectra were recorded either on a *Cary* model 14 or on a *Durrum* prism-grating model PGS spectrophotometer; 1 cm cells were used. Specially constructed anaerobic cells were used for reduction processes as described previously [20]. NMR. spectra were recorded on a *Varian* T 60 spectrometer using tetramethylsilane as internal standard. Chemical shift values are expressed as δ in ppm. Plates of MN-polygram SIL S-HR (starch as binder) from *Macherey-Nagel & Co.* (Düren, Germany) were used for thin layer chromatography (TLC.); the best separation of the compounds described was obtained by using benzene-chloroform-ethanol (25:25:1) as eluant. All solvents used were reagent grade; glass-distilled water was used for preparation of all aqueous solutions; lithium borohydride (99%) was an *Alfa Inorganics Inc.* product; 5-aminouracil and alloxan monohydrate were obtained from *Eastman Organic Chemicals;* 4,5-dimethyl-2-nitro-aniline from *Aldrich Chemical Co., Inc.* The pK values were determined spectrophotometrically in 0.1 M phosphate buffer solutions. If not otherwise stated, experiments were carried out at 23–25°.

N(3)-Benzylriboflavin (**3a**): A suspension of 1.0 g of N-benzylbarbituric acid (**2a**) [21] and 1.5 g of 2-D-ribitylamino-4,5-dimethyl-azobenzene[3]) (**1**), in 15 ml of glacial acetic acid and 20 ml of *n*-butanol, was heated under reflux for 2.5 h, during which time **3a** crystallized as straw-yellow needles. The mixture was cooled to 25°, and **3a** (1.32 g, 53%), m.p. 276–277°, was filtered off and washed thoroughly with alcohol and ether. For analysis, **3a** was recrystallized from dimethylformamide.

$C_{24}H_{26}N_4O_6$ (475.5) Calc. C 61.8 H 5.6 N 12.0% Found C 61.2 H 5.7 N 11.8%

N(3)-Benzyl-7,8-dimethyl-10-formylmethyl-isoalloxazine (**4a**): A suspension of 1.0 g of **3a** in 100 ml of 50% (*v/v*) aqueous acetic acid containing 0.4 g of periodic acid was stirred at 25° for 2.5 h, protected from light. The nearly clear red-brown solution was treated with activated charcoal and

[3]) Gift from *Hoffmann-La Roche AG, Basel.*

filtered. Aqueous ammonia was added to the filtrate, with stirring and under cooling, until the first crystals appeared on the wall of the reaction vessel. Concentrated aqueous ammonia was added dropwise to complete the precipitation; the product was filtered off, washed thoroughly with water, alcohol, and ether; 0.66 g (81%) of **4a**, m.p. 208–209°. The compound was recrystallized twice from 2N acetic acid for analysis.

$C_{21}H_{18}N_4O_3, 1.5\,H_2O$ (401.4) Calc. C 62.8 H 5.2 N 13.9% Found C 62.8 H 5.0 N 13.8%

N(3)-Benzyl-7,8-dimethyl-alloxazine (**5a**): 1.0 g of **4a** was dissolved in 25 ml of hot glacial acetic acid, 5 ml of 30% hydrogen peroxide were added, and the mixture heated under reflux for 30 min; the colour of the solution changed from orange-red to yellow. An equal volume of water was added, the solution was allowed to cool and then kept at 6° for 12 h. The pale yellow crystalline product (prisms, 0.56 g, 74%), m.p. > 360°, was filtered off and washed successively with water, alcohol, and ether. Compound **5a** was recrystallized twice from 50% acetic acid for analysis. – NMR.-spectrum (in CF_3COOD): 8.18 (1H, singlet, [C(6)—H]); 7.97 (1H, singlet, [C(9)—H]); 7.35 (5H, multiplet, [N(3)—C_6H_5]); 5.43 (2H, singlet, [N(3)—CH_2]); 2.72 (3H, singlet, [C(8)—CH_3]); 2.68 (3H, singlet, [C(7)—CH_3]). – IR. spectrum: νNH(1) 3200; νCO(4) 1732, νCO(2) 1675 cm^{-1}.

$C_{19}H_{16}N_4O_2 \cdot H_2O$ (350.4) Calc. C 65.4 H 5.1 N 15.9% Found C 65.3 H 4.9 N 15.9%

N(1)-Methyl-N(3)-benzyl-7,8-dimethylalloxazine (**6**): To a stirred suspension of 1.0 g of **5a** and 2.8 g of potassium carbonate in 30 ml of dimethylformamide at 60°, a 10 ml mixture (1:1, *v/v*) of dimethylsulfate/dimethylformamide was added during 30 min; stirring was continued for a further 30 min. The mixture was then evaporated to dryness at 60° under reduced pressure; the residue was suspended in chloroform, the organic phase washed with 0.1N sodium hydroxide and then repeatedly with water. After drying (anhydr. sodium sulfate) the chloroform solution was evaporated to give a solid residue (0.85 g, 82%), which was recrystallized from aqueous ethanol to give yellow needles of **6**, m.p. 225°. IR. spectrum: νCO(4) 1720 and νCO(2) 1675 cm^{-1}.

$C_{20}H_{18}N_4O_2$ (346.4) Calc. C 69.3 H 5.2 N 16.1% Found C 69.6 H 5.3 N 16.0%

N(1),7,8-Trimethylalloxazine (**7**): The N(3)-benzyl group of **6** (100 mg) was removed by 30 min treatment with a solution of 50 mg of sodium in 30 ml of ammonia. 135 mg of solid ammonium chloride were then added and the ammonia was allowed to evaporate. To the residue 1 ml of alcohol and 10 ml of 2N acetic acid were added successively; the insoluble product was filtered off and recrystallized from alcohol, yielding 30 mg (41%) of **7**, yellow prisms, m.p. > 300°. – NMR. spectrum (in CF_3COOD): 8.20 (2H, singlet, [C(6)—H and C(9)—H]); 4.00 (3H, singlet, [N(1)—CH_3]);

Table II. *Ultraviolet and visible light absorption maxima and minima of N(1),7,8-trimethylalloxazine* (**7**)

pH 6.3[a]				pH 13[b]			
maxima		minima		maxima		minima	
λ nm	$\varepsilon \times 10^{-3}$	λ nm	$\varepsilon \times 10^{-3}$	λ nm	$\varepsilon \times 10^{-3}$	λ nm	$\varepsilon \times 10^{-3}$
388	7.92	378	7.70	395	10.1	368	8.08
355	10.7	288	1.00	347	10.0	288	2.20
253	38.8	230	16.7	256	48.4	232	14.3
216	34.4			212	34.4		
6N HCl				Methanol			
maxima		minima		maxima		minima	
λ nm	$\varepsilon \times 10^{-3}$	λ nm	$\varepsilon \times 10^{-3}$	λ nm	$\varepsilon \times 10^{-3}$	λ nm	$\varepsilon \times 10^{-3}$
393	10.4	370	9.07	386	8.12	363	6.62
363	9.23	300	0.94	340	8.40	285	0.63
265	36.4	242	20.5	250	39.0	230	14.3
				218	36.5		

[a] 0.1M phosphate buffer. [b] 0.1N sodium hydroxide.

2.73 (6H, singlet, [C(8)—CH_3 and C(7)—CH_3]). – IR. spectrum: νNH(3) 3200, νCO(4) 1725, νCO(2) 1690 cm^{-1}.

$C_{13}H_{12}N_4O_2$ (256.3) Calc. N 21.8 N(CH_3) 5.8% Found N 21.9 N(CH_3) 5.6%

N(3),7,8-Trimethylalloxazine (**5b**) was synthesized virtually by the route described for **5a** except for a difference in procedure for the periodate oxidation of the intermediate N(3)-methylriboflavin (**3b**). N(3)-Methylriboflavin was synthesized by the procedure of *Föry & Hemmerich* [11]. Periodate oxidation of **3b** was carried out according to *Fall & Petering* [12], but employing 2N sulfuric acid instead of aqueous acetic acid, and adjusting the pH to 2.0 instead of 3.8. After maintaining at 6° for 12 h, a precipitate was filtered off and discarded; the filtrate was treated with charcoal and, after filtration, the pH of the solution was adjusted to 4.0. After 12 h. at 6° **5b** separated in 60% yield. For analysis the compound was recrystallized from methanol (yellow microcrystalls, m.p. > 300°). – NMR. spectrum (in CF_3COOD): 8.19 (1H, singlet, [C(6)—H]); 8.0 (1H, singlet, [C(9)—H]); 3.70 (3H, singlet [N(3)—CH_3]); 2.72 (3H, singlet, [C(8)—CH_3]); 2.68 (3H, singlet, [C(7)—CH_3]). – IR. spectrum: νNH(1) 3200, νCO(4) 1720, νCO(2) 1675 cm^{-1}.

$C_{13}H_{12}N_4O_2$ (256.3) Calc. C 60.6 H 4.6 N 21.7% Found C 59.8 H 4.6 N 21.4%

Table III. *Ultraviolet and visible light absorption maxima and minima of N(3),7,8-trimethylalloxazine* (**5b**)

pH 6.3[a]				pH 13[b]			
maxima		minima		maxima		minima	
λ nm	$\varepsilon \times 10^{-3}$	λ nm	$\varepsilon \times 10^{-3}$	λ nm	$\varepsilon \times 10^{-3}$	λ nm	$\varepsilon \times 10^{-3}$
388[c]	7.90	298	2.53	428	7.90	378	2.90
355	11.2	243	12.0	345	6.63	307	2.42
258	37.9			265	44.7	237	13.1
6N HCl				Methanol			
maxima		minima		maxima		minima	
λ nm	$\varepsilon \times 10^{-3}$	λ nm	$\varepsilon \times 10^{-3}$	λ nm	$\varepsilon \times 10^{-3}$	λ nm	$\varepsilon \times 10^{-3}$
390	13.0	300	1.25	388	7.72	363	6.23
263	36.8	242	18.9	340	8.40	288	1.25
				252	35.7	230	14.2

[a] 0.1M phosphate buffer. [b] 0.1N sodium hydroxide. [c] Shoulder.

1,3,7,8-Tetramethyl-4,4O-dihydro-alloxazine (**9**): To a suspension of 200 mg of lithium borohydride in 50 ml of absolute ether at 6° (ice-water bath), a suspension of 250 mg of **8** in 50 ml of absolute methanol was added during 10 min. The cold (6°) mixture was stirred for 30 min, the ice-water bath removed, and stirring continued for a further 30 min after which time an almost clear solution resulted. A sample submitted to TLC. indicated the presence of very little starting material (blue fluorescent zone) and a single new zone (purple fluorescent). The solvent was evaporated under reduced pressure at 30°, the residue suspended in water to dissolve inorganic material, and **9** (220 mg, 87%) was filtered off, dried (60°, 12 h), and recrystallized from methanol to give colorless needles, m.p. 241–242.5°. – NMR. spectrum (in CF_3COOD): 8.09 (2H, singlet, [C(6)—H and C(9)—H]); 4.16 (3H, singlet, [N(3)—CH_3]); 4.29 (3H, singlet, [N(1)—CH_3]); 2.75 (3H, singlet, [C(8)—CH_3]); 2.68 (3H, singlet, [C(7)—CH_3]). – IR. spectrum: νOH(4) 3165, νCH(4) 2930, νCO(2) 1690, νCOH(4) 1004 cm^{-1}.

$C_{14}H_{16}N_4O_2$ (272.3) Calc. C 61.60 H 5.88 N 20.50% Found C 61.48 H 5.84 N 20.34%

After further recrystallization of **9** from methanol, TLC. showed besides **9** an additional faster moving, very weakly fluorescent zone, the intensity of which increased with each further recrystallization of **9**. The new zone was identified as **11** by comparison of its TLC. properties with those of authentic material described below.

7,8-Dimethyl-4-O-methyl-4,4O-dihydro-alloxazine (**11**): 100 mg of **9** were dissolved in hot absolute methanol (30 ml), three drops of 12N hydrochloric acid were added, and the yellow solu-

tion was kept overnight at ambient temperature. After evaporation of the solvent under reduced pressure at 15–20°, the oily residue was suspended in water, the suspension was neutralized with solid sodium hydrogen carbonate and extracted with 2 × 20 ml of chloroform. The combined organic extract was dried (anhydr. sodium sulfate) and evaporated to dryness. The residue was dissolved in a hot mixture of 5 ml of methanol and 1 ml of chloroform; this solution was left standing for 4 h at ambient temperature and then 12 h at 6°. **11** (80 mg, 76%) was obtained as colorless needles, m.p. 137.5–139°. IR. spectrum: νCH(4) 2915, νCO(2) 1675, and $\nu COCH_3$(4) 1062 cm^{-1}.

$C_{15}H_{18}N_4O_2$ (286.3) Calc. C 62.80 H 6.28 N 19.55% Found C 62.82 H 6.31 N 19.44%

7,8-Dimethyl-4,4O-dihydro-alloxazine (**12**): 4,5-Dimethyl-2-nitro-aniline (500 mg) was dissolved in 150 ml of glacial acetic acid and hydrogenated at atmospheric pressure (25°), over 5% palladium-charcoal, to yield the corresponding orthodiamine. After filtration from the catalyst, isodialuric acid [22] (750 mg) was added. The solution was then thoroughly deaerated with nitrogen, stirred for 4 h at 25° (under N_2), and the resulting mixture left to stand at 6° for 12 h. The pale greenish yellow precipitate of **12** (0.48 g, 66%) was filtered off and washed with ether. A sample was

Table IV. *Ultraviolet and visible light absorption maxima and minima of N(1),N(3),7,8-tetramethyl-4,4O-dihydroalloxazine* (**9**)

pH 6.5[a]				pH 13[b]			
maxima		minima		maxima		minima	
λ nm	$\varepsilon \times 10^{-3}$	λ nm	$\varepsilon \times 10^{-3}$	λ nm	$\varepsilon \times 10^{-3}$	λ nm	$\varepsilon \times 10^{-3}$
360	11.5	285	1.55	355	13.6	285	2.88
252	27.6	228	9.80	258	29.6	243	16.4
216	33.6						
5 N HCl				Methanol			
maxima		minima		maxima		minima	
λ nm	$\varepsilon \times 10^{-3}$	λ nm	$\varepsilon \times 10^{-3}$	λ nm	$\varepsilon \times 10^{-3}$	λ nm	$\varepsilon \times 10^{-3}$
380	12.7	300	1.22	360	11.6	285	2.73
264	31.2	232	7.55	250	29.7	228	13.9
215	31.2			216	41.2		

[a] 0.1 M phosphate buffer. [b] 0.1 N sodium hydroxide.

Table V. *Ultraviolet and visible light absorption maxima and minima of 7,8-dimethyl-4,4O-dihydro-alloxazine* (**12**)

pH 6.5[a]				pH 13[b]			
maxima		minima		maxima		minima	
λ nm	$\varepsilon \times 10^{-3}$	λ nm	$\varepsilon \times 10^{-3}$	λ nm	$\varepsilon \times 10^{-3}$	λ nm	$\varepsilon \times 10^{-3}$
358	9.65	280	1.22	377	10.4	308	2.23
257	29.2	227	11.6	270	24.6	240	9.90
213	34.2						
5 N HCl				Methanol			
maxima		minima		maxima		minima	
λ nm	$\varepsilon \times 10^{-3}$	λ nm	$\varepsilon \times 10^{-3}$	λ nm	$\varepsilon \times 10^{-3}$	λ nm	$\varepsilon \times 10^{-3}$
376	12.6	293	0.56	355	9.30	278	1.50
262	24.2	228	7.55	256	29.6	227	12.8
214	28.0			214	37.8		

[a] 0.1 M phosphate buffer. [b] 0.1 N sodium hydroxide.

prepared for analysis by adding an equal volume of water to its hot dimethylformamide solution which was left at 6° for 4 h; pale yellow powder, m.p. > 300°. – NMR. spectrum (in CF_3COOD): 8.10 (1H, singlet, [C(6)–H]); 7.87 (1H, singlet, [C(9)–H]; 2.65 (6H, singlet, [C(8)–CH_3 and C(7)–CH_3]). – IR. spectrum: νOH(4) 3210, νNH(1,3) 3100, νCO(2) 1688, νCOH(4) 1005 cm^{-1}.

$C_{12}H_{12}N_4O_2 \cdot H_2O$ (262.2) Calc. C 54.70 H 5.30 N 21.30% Found C 54.47 H 5.38 N 20.89%

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158. Etude de la séparation de traces de mercure ionique par adsorption, en milieu aqueux, sur verre sodocalcique. Application à la séparation Hg^{2+}-organomercuriels

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Summary. The separation conditions of traces of ionic mercury from aqueous solution on microbeads of soda lime are studied theoretically and established experimentally. The formation of a stable complex of the ion with ethylene diamine allows to operate at pH 7–8. The efficiency of

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