Photochemical Dehydrogenation, Ring Contraction, and Ring Expansion of Hydrogenated Derivatives of Benzoxazino-benzoxazine, Quinoxalino-quinoxaline, and Bibenzothiazole

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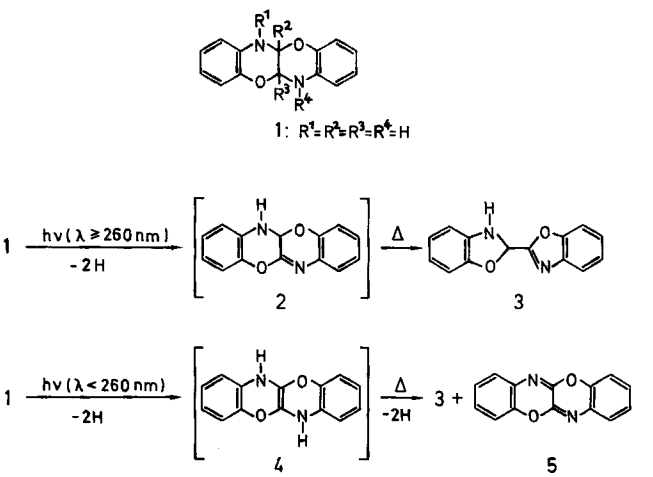
The photochemical properties of the title compounds have been investigated and compared. The benzoxazino-benzoxazine derivatives **1** are photochemically converted into hydrogenated oxazole derivatives. In some cases this ring contraction is accompanied by a dehydrogenation reaction whereby the heterocyclic ring system becomes aromatic. Hydrogenated quinoxalino-quinoxalines also undergo a photodehydrogenation reaction and become aromatic. However, a ring contraction yielding the imidazolyl system does not take place. The only investigated sulfur-containing analog has different properties. The stable form is the bibenzothiazole **23** which contains a five-membered heterocyclic ring system. Photochemically **23** rearranges under ring expansion to give the benzothiazino-benzothiazine **24**.

As we have shown recently, the condensation of 2-aminophenol with glyoxal (molar ratio 2:1) yields 5a,6,11a,12-tetrahydro[1,4]benzoxazino[3,2-*b*][1,4]benzoxazine (**1**), whose structure has been verified by X-ray analysis[1]. This compound has interesting photochemical properties which depend on the wavelength of the exciting light. Irradiation of an air-equilibrated solution of **1** in an alkane solvent (CH), with light of wavelength $\lambda \geq 260$ nm yields the dihydrobibenzoxazole **3** with 12% chemical yield. Short-wavelength excitation ($\lambda < 260$ nm) also leads to the formation of **3** but, in addition, [1,4]benzoxazino[3,2-*b*][1,4]benzoxazine (**5**) is produced in 4% chemical yield (Scheme 1). Evidently, only short-wavelength excitation affords a photoproduct in which the four six-membered ring system of the parent compound **1** is still intact, but rearrangement to bibenzoxazole-like structures occurs apparently with much higher efficiency.

Scheme 1



	R^1	R^2	R^3	R^4
1	H	H	H	H
1a	H	H	CH_3	CH_3
1b	CH_3	H	H	H
1c	C_6H_5	H	H	H
1d	CH_3	CH_3	H	H
1e	C_6H_5	C_6H_5	H	H
1f	CH_3	C_6H_5	H	H

In Scheme 1 we assume that the primary photooxidation product has the structure **2** in the reaction path **1** → **3**, and structure **4** in the "short-wavelength" path **1** → **5**. The first stable photoproduct, **3**, of the "long-wavelength" pathway is formed after the absorption of one photon under elimination of two hydrogen atoms. (The absorption of a second photon is required to convert **3** into the oxidation product bibenzoxazole.) In the other route, absorption of just one photon yields as the first stable photoproduct the benzoxazino-benzoxazine **5** where four hydrogen atoms have been eliminated. The second step in this reaction (**4** → **5**) is presumably a thermal reaction. Neither **2** nor **4** could be detected directly.

In this paper we discuss some experimental results obtained with compounds related to **1**. In the first group of these compounds the hydrogen atoms at the central carbon atoms (R^1, R^2) or at the nitrogen atoms (R^3, R^4) are replaced by substituents. In the second group, the oxygen atoms of **1** are replaced by NH, NCH_3 or S. The purpose of these modifications was originally to reduce the number of photooxidizable hydrogen atoms of **1** at selected sites in the hope to obtain photoproducts with structures related to the hypothetical intermediates **2** and **4**, in order to put their postulation on firmer grounds. These efforts were awarded only with modest success. It turned out that the investigated

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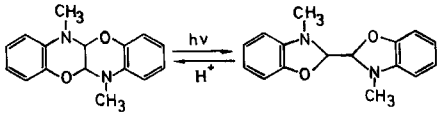
derivatives and analogs of **1** have in part rather unexpected photochemical properties a number of which are described in this paper.

Modification of the NH Groups of 1

If in the parent compound **1** the hydrogen atoms R^3 and R^4 are replaced by $R^3 = R^4 = CH_3$, no photooxidation at the central C–C bridge takes place with appreciable yield, i.e. the *N*-methylated analogon to **4** (Scheme 1) could not be detected. Instead, **1a** (Scheme 2) rearranges to 2,2′,3,3′-tetrahydro-3,3′-dimethyl-2,2′-bibenzoxazole (**6**). The chemical yield is 70% in degassed cyclohexane (CH). In air-equilibrated CH the yield is much lower (3–5%) and side reactions take place, which have not been investigated in detail. The yield of the reaction **1a** → **6** is independent of the wavelength of the exciting light both in degassed and air-equilibrated solution. In the crystalline state and in neutral solution, **6** is a stable compound. Traces of acids in solvents like ethanol or chloroform reconvert **6** quickly into **1a**. (This can cause problems if NMR spectra of **6** are taken in $CDCl_3$ as solvent which may contain hydrochloric acid.)

Scheme 2



1a 6

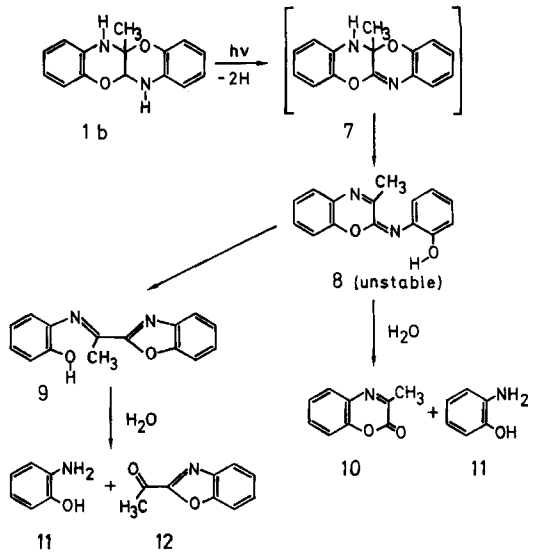
Modification at the Central C–C Bridge of 1

On irradiation of a degassed solution of **1b** ($\approx 10^{-4}$ M) in CH a compound with two absorption maxima at $\lambda = 375$ and 390 nm is formed. On standing in the dark, this spectrum does neither change in the presence nor in the absence of oxygen. If the solution is concentrated by evaporation of the solvent under reduced pressure or with a stream of nitrogen, the absorption spectrum changes irreversibly and the absorption maximum at $\lambda = 390$ nm disappears. The finally isolated photoproduct 2-[1-(2-benzoxazolyl)ethylideneamino]phenol (**9**) shows an absorption maximum at 375 nm. It was identified by comparison with an authentic sample (mixed melting point). Presumably, the primary photooxidation product of **1b** is the benzoxazine derivative **7**, as indicated in Scheme 3. However, benzoxazines of this type absorb at wavelengths shorter than 390 nm. We therefore assume that **7** rearranges quickly to **8** which has an extented conjugated π-electron system.

A solution of **8** in CH is hydrolyzed by addition of a small amount of water. In agreement with the proposed structure of **8**, the hydrolysis products are 3-methyl-2*H*-1,4-benzoxazin-2-on (**10**) and 2-aminophenol (**11**). The hydrolysis of **9**, on the other hand, yields 1-(2-benzoxazolyl)ethanon (**12**) and **11** (cf. Scheme 3).

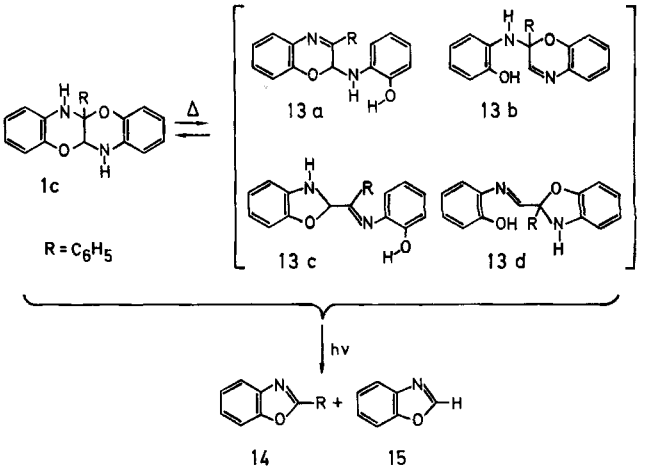
In **1c** the 5a-methyl group of **1b** is replaced by a phenyl group. The result of this substitution is a drastic change of the chemical and photochemical properties. A freshly prepared solution of **1c** in CH has an absorption spectrum with

Scheme 3



a maximum at $\lambda = 289$ nm and an extinction coefficient at this wavelength of $\varepsilon(289) = 8370\ M^{-1}\ cm^{-1}$. On standing at room temperature, a second absorption maximum at 315 nm develops with a "half life" of about 45 min. This process is reversible: If the solvent is removed by evaporation, **1c** recrystallizes and exhibits the spectrum of the freshly prepared solution if the recovered crystals are dissolved again. In analogy to the findings of Belgodere et al.[2] who investigated the condensation products of 2-aminophenol and α-dicarbonyl compounds, we assume that this change of the absorption spectrum is due to the formation of one isomer or an equilibrium of several isomers, the possible structures of which are shown in Scheme 4.

Scheme 4



Irradiation of a degassed or of an air-equilibrated solution of **1c** in CH yields as main products 2-phenylbenzoxazole (**14**) and benzoxazole (**15**). The irradiation time was considerably longer ($\approx 8-24$ h) than the time needed to establish the equilibrium **1c** ⇌ **13** (Scheme 4). In degassed solution a small amount of a compound is formed which has two

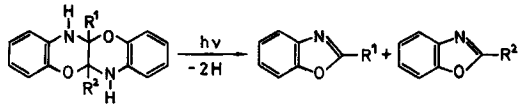
absorption maxima at 390 and 410 nm. It is presumably the analog of **8** (cf. Scheme 3). The benzoxazoles **14** and **15** are not formed in equal chemical yields (cf. Table 1), the yields depending on the excitation wavelength.

Table 1. Chemical yield of 2-phenylbenzoxazole (**14**) and benzoxazole (**15**) obtained by irradiation of 10^{-4} M solutions of **1c** in CH. The yields were determined from the absorption spectra of the irradiated solutions.

Excitation wavelength [nm]	% Chemical yield Air-equilibrated 2-Phenylbenzoxazole	Air-equilibrated Benzoxazole	Degassed 2-Phenylbenzoxazole	Degassed Benzoxazole
254	18	9	18	11
≥280	31	11	30	10

Replacement of *both* central 5a,11a-hydrogen atoms of **1** by methyl (**1d**), phenyl (**1e**) or methyl- and phenyl groups (**1f**) yields derivatives which, in contrast to the 5a-phenyl derivative **1c** do not isomerize in solution. However, similar to **1c** (cf. Scheme 4) irradiations of solutions of **1d**, **1e** and **1f** in CH (degassed or air-equilibrated) led to the formation of 2-substituted benzoxazoles, as shown in Scheme 5. The photoproducts were chromatographically separated and identified by comparison with the UV spectra and the GC and TLC retention times of authentic samples.

Scheme 5



1d: $R^1=R^2=CH_3$ ——— 16 + 16
1e: $R^1=R^2=C_6H_5$ ——— 14 + 14
1f: $R^1=CH_3, R^2=C_6H_5$ ——— 16 + 14

The chemical yields of the formation of **14** and 2-methylbenzoxazole (**16**) were estimated (cf. Table 2) by irradiation of 1×10^{-4} M solutions of **1d**, **1e** or **1f** until the characteristic benzoxazole UV-absorption peaks ceased to develop further. The values obtained by this method are not very accurate, but they show that the formation of 2-R-benzoxazoles depends on the wavelength of excitation as well as on the substituent R.

Table 2. Chemical yield (%) of 2-methylbenzoxazole and/or 2-phenylbenzoxazole obtained by photoreaction of compounds **1d**, **1e** and **1f**

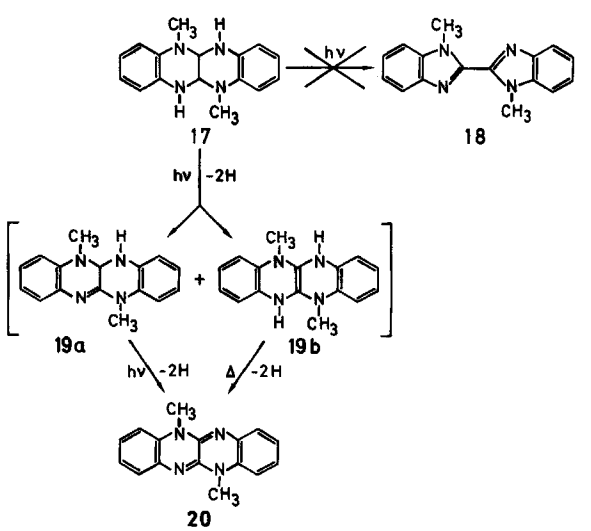
Product	(Exc.) [nm]	Compound 1d Degassed	1d Air-equilibrated	1e Degassed	1e Air-equilibrated	1f Degassed	1f Air-equilibrated
2-Methyl-benzoxazole	254	9	4	–	–	28	21
	≥280	11	9	–	–	64	43
2-Phenyl-benzoxazole	254	–	–	30	22	29	16
	≥280	–	–	56	41	55	37

Quinoxalino-quinoxalines

The condensation product of *N*-methyl-*o*-phenylenediamine and glyoxal, **17**, is a stable compound like **1**. However, in contrast to **1** (cf. Scheme 1) only one photodehydrogenation product is formed from **17**, namely 5,11-dimethylquinoxalino[2,3-*b*]quinoxaline (**20**). In air-equilibrated CH as solvent the chemical yield is independent of the excitation wavelength (254 and ≥ 280 nm) and quite high (≈ 80%) provided only small amounts of the solute are converted, i.e. as long as the photoproduct does not appreciably absorb the exciting light. In degassed CH the yield is lower (≈ 60%) under short-wavelength (254 nm) excitation. Like **5**, the photoproduct has characteristic absorption peaks with maxima at λ_{max} = 368, 388, 411 and 437.5 nm and it fluoresces with high quantum yield (λ_{max} = 442, 472, 506, 544 and 590 nm). Surprisingly (cf. Scheme 1), 3,3′-dimethyl-2,2′-bibenzimidazole (**18**) is not formed in detectable amounts. (Limit of detection ≈ 0.5%; **18** has strong absorption peaks at 327 and 344.5 nm, where the extinction coefficients of **17** are almost zero.) This is quite in contrast to the case of benzoxazino-benzoxazine **1** where the rearrangement of its six-membered ring system to the five-membered ring system of **3** is the main photoreaction pathway.

If one monitors the formation of **20** by measuring the absorbance at a given wavelength $E(\lambda)$ as a function of irradiation time t, an increase of the rate of formation $[\Delta E(\lambda)/\Delta t]$ is observed at the beginning of the photoreaction. After this induction period, the rate of formation remains constant (provided, of course, that the light absorption has not yet decreased appreciably due to the consumption of starting material). If the irradiation is interrupted for a certain period, the absorbance at the monitoring wavelength still increases further to a final value within a "half life" of about 3 h. If the excitation is continued after this interruption, the rate of formation is the same as before the

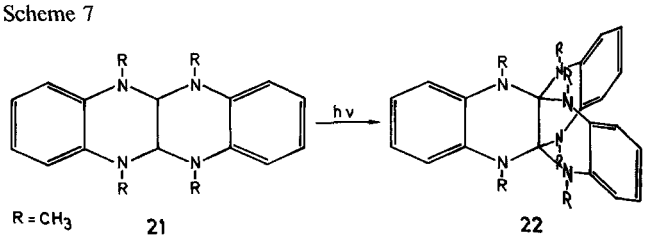
Scheme 6



interruption, i.e. the photoreaction continues *without* a new induction period. An unexposed, dark-stored solution does not change its absorbance.

From these observations we conclude that, in analogy to Scheme 1, two intermediates are formed photochemically: One (labeled **19a** in Scheme 6) which has to absorb a second photon to be converted into **20** and another one (**19b**) which is slowly thermally converted into **20**.

Scheme 7

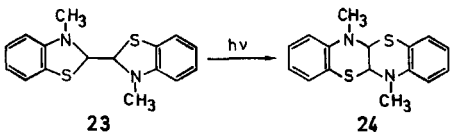


The most surprising photochemical properties exhibits the tetramethyl-substituted derivative **21** as we reported in a short communication[3]. Compound **21** is converted into the propellan-type product **22** in relatively high chemical yield (11%) by irradiation of a nitrogen-purged solution of **21** in cyclohexane with a mercury resonance lamp (λ = 254 nm) (Scheme 7).

The propellane structure of **22** (orthoamide of oxalic acid) has been verified by X-ray analysis[3]. To our knowledge no oxalic acid orthoamide has so far been described in the literature. Besides **22**, a large number of other unidentified photoproducts are formed from **21** in smaller yields.

2,2'-Bibenzothiazole 23

In contrast to all other derivatives of **1** described in this paper, condensation of 1 mol of glyoxal with 2 mol of *N*-methyl-2-aminothiophenol does not yield a benzothiazinobenzothiazine but the bibenzothiazole **23**. The structure of **23** follows from its mass spectrum which shows a peak at the molecular mass (m/z = 300, M^+) and, as fragment with the highest mass, a peak at $M^+/2$ (m/z = 150). Irradiation of a degassed solution of **23** in CH yields the [1,4]benzothiazino[3,2-*b*]benzothiazine **24**. The NMR and UV spectra of starting material and photoproduct are very similar and the elementary analysis shows that the molecular formula of the photoproduct is the same as that of the starting material. The mass spectrum of **24**, however, exhibits besides the M^+ (m/z = 300) and $M^+/2$ (m/z = 150) peaks two fragments which are 13 mass units (C + H) larger or smaller than $M^+/2$. We have observed such fragments only in ring systems like **1**. Analogous to **1a** (cf. Scheme 2) photooxidation of **23** does not take place with appreciable yield and the rearrangement **23** → **24** proceeds with a much lower yield in an air-equilibrated CH solution.



We thank Mrs. *A. Heinrich* for technical assistance.

Experimental

Spectra: UV: Perkin-Elmer Model 320. – Fluorescence: Spex Fluorolog. – ^{1}H NMR: Bruker WH 270. – MS: Varian MAT CH 17. – Melting points were determined in open capillaries and are uncorrected. – Irradiation experiments were carried out with 10^{-4} M solutions. The solutions were degassed by purging with purified nitrogen (< 2 ppm O_2). For "short-wavelength" irradiations (254 nm) a low-pressure, 15-W mercury lamp (Hanau NN 15/44) was employed and for "long-wavelength" irradiations a medium pressure, 50-W mercury lamp (Osram Hg 100) together with a cut-off filter (Schott WG 280). For irradiations on a preparative scale a Rayonet reactor with 16 lamps (254 nm) was used and the concentration of the solutions was about 5×10^{-3} M. – The solvent used was cyclohexane (CH) (Uvasol quality, Merck-Schuchardt, or for preparative irradiations Baker, p.a.).

5a,6,11a,12-Tetrahydro-6,12-dimethyl[1,4]benzoxazino[3,2-b][1,4]benzoxazine (**1a**): 24.6 g (0.2 mol) of 2-(methylamino)phenol[4] was dissolved under nitrogen in 100 ml of ethanol, 19.3 g (0.1 mol) of glyoxal (30% in H_2O) was added and the solution was heated at reflux for 1 h. After cooling, the product was filtered, washed with a little ethanol and dried; yield 11.55 g (43%), m.p. 159–163°C. Further purification on an Al_2O_3 column (eluant CH/diisopropyl ether, 3:1 by vol.) and recrystallization from ethanol yielded colorless needles, m.p. 163–164°C. – UV (CH): λ_{max} (lgε) = 292 nm (3.88), 259 (4.15), 211 (4.86). – ^{1}H NMR ($CDCl_3$): δ = 3.2 (s, 6H, CH_3), 5.25 (s, 2H, CH), 6.6–7.0 (m, 8H, arom. H).

$C_{16}H_{16}N_2O_2$ (268.3) Calcd. C 71.62 H 6.01 N 10.44 O 11.93
Found C 71.66 H 6.12 N 10.50 O 11.84

5a,6,11a,12-Tetrahydro-5a-methyl[1,4]benzoxazino[3,2-b][1,4]benzoxazine (**1b**) was prepared according to Murase[5]; m.p. 218–219°C (from ethanol). The MS and the X-ray structure of **1b** have been determined by Barluenga et al.[6].

5a,6,11a,12-Tetrahydro-5a-phenyl[1,4]benzoxazino[3,2-b][1,4]benzoxazine (**1c**): 22 g (0.2 mol) of 2-aminophenol and 15.2 g (0.1 mol) of phenylglyoxal hydrate were dissolved in 150 ml of toluene and boiled in a Dean-Stark trap until 4.5 ml (theoretical value 5.4 ml) of H_2O had separated. On cooling, colorless crystals separated [20.2 g (64%), m.p. 154–155°C], after recrystallization from ethanol m.p. 160–161°C (ref.[2a] 155–157°C).

5a,6,11a,12-Tetrahydro-5a,11a-dimethyl[1,4]benzoxazino[3,2-b][1,4]benzoxazine (**1d**) was prepared according to Kehrmann[7]; m.p. (from ethanol) 240–241°C. An X-ray structure of **1d** has been reported by Barluenga et al.[6]. – UV (CH): λ_{max} (lgε) = 289 nm (3.93), 230 (sh) (4.10), 207 (4.94).

5a,6,11a,12-Tetrahydro-5a,11a-diphenyl[1,4]benzoxazino[3,2-b][1,4]benzoxazine (**1e**): 22 g (0.2 mol) of 2-aminophenol and 21 g (0.1 mol) of benzil were dissolved in 150 ml of toluene and boiled in a Dean-Stark trap until 2.9 ml (0.16 mol) of H_2O had separated (≈ 2 d). After cooling, 100 ml of toluene was evaporated from the reaction mixture, the residue diluted with 150 ml of ethanol and allowed to stand for ≈ 12 h. Filtration of the precipitate and washing with ethanol yielded 15.1 g (39%) of crude **1e** (m.p. ≈ 206°C), which was recrystallized twice from ethanol to yield colorless crystals with m.p. 211–212°C. – UV (CH): λ_{max} (lg ε) = 287 nm, (4.02). – ^{1}H NMR ($CDCl_3$): δ = 4.75 (s, 2H, NH), 6.6–7.4 (m, 18H, arom.). – MS (70 eV): m/z (%) = 392 (31) [M^+], 285 (43), 284 (45), 196 (100), 195 (100).

$C_{26}H_{20}N_2O_2$ (392.5) Calcd. C 79.57 H 5.14 N 7.14 O 8.15
Found C 79.38 H 5.21 N 7.13 O 8.33

5a,6,11a,12-Tetrahydro-5a-methyl-11a-phenyl[1,4]benzoxazino[3,2-b][1,4]benzoxazine (**1f**) was prepared according to Murase[5];

m.p. (from ethanol) 218°C. The X-ray structure of **1f** has been determined by Barluenga et al.[6]. – UV (CH): λ_{max} (lgε) = 288 nm (3.97), 207 (4.99).

2-[1-(2-Benzoxazolyl)ethylideneamino]phenol (**9**). – A) *1-(2-Benzoxazolyl)ethanol:* 66 g (0.6 mol) of 2-aminophenol and 60 g (0.6 mol) of d,l-lactic acid (90% in water) were heated under stirring on an oil bath to 140°C until 16.5 ml of H_2O was formed (≈ 4 h). Without allowing to cool down the liquid crude product was distilled with a Vigreux column (140°C, 13 Torr). The distillate was again distilled with a Widmer column yielding 72.0 g (74%) of a nearly colorless, viscous oil, b.p. 137°C (13 Torr). – ^{1}H NMR ($CDCl_3$): δ = 1.73 (d, *J* = 5 Hz, 3H, CH_3), 4.30 (s, 1H, OH), 5.15 (q, *J* = 5 Hz, 1H, C*H*OH), 7.15–7.8 (m, 4H, arom. H).

$C_9H_9NO_2$ (163.2) Calcd. C 66.25 H 5.56 N 8.58 O 19.61
Found C 66.34 H 5.58 N 8.60 O 19.75

B) *1-(2-Benzoxazolyl)ethanone* (**12**) was prepared analogously to the method of Pratt et al.[8]. 135 g (1.5 mol) of MnO_2 (freshly precipitated) was suspended in 1.5 l of CH, 49 g (0.3 mol) of 1-(2-benzoxazolyl)ethanol was added, and the mixture was boiled in a Dean-Stark trap for 16 h under vigorous stirring. After cooling, the reaction mixture was separated from MnO_2 and after evaporation of the solvent 44 g of a dark oil remained. This oil was distilled with a Widmer column (13 Torr) until a boiling point of 137°C was reached. The distillate (≈ 15 g) was collected in a saber-shaped flask and chromatographed on a silica column with CH/diethyl ether (1:1) as eluant. Recrystallization from CH yielded 9.2 g (19%) of **12** as colorless crystals with m.p. 80–81°C. – ^{1}H NMR ($CDCl_3$): δ = 2.8 (s, 3H, CH_3), 7.35–7.95 (m, 4H, arom. H).

$C_9H_7NO_2$ (161.2) Calcd. C 67.08 H 4.38 N 8.69 O 19.86
Found C 67.19 H 4.47 N 8.68 O 19.76

C) 4.02 g (25 mmol) of **12** and 2.37 g (25 mmol) of 2-aminophenol were dissolved in 50 ml of toluene and boiled in a Dean-Stark trap until ≈ 0.3 ml (17 mmol) of water had separated. After evaporation of the solvent the reaction mixture was chromatographed on a silica column with CH/diisopropyl ether (1:1), yielding 4.08 g (68%) of crude product. After recrystallization from toluene 1.28 g (20.3%) of **9** was obtained as yellow crystals, m.p. 127–128°C. – UV (CH): λ_{max} (lgε) = 374 nm (3.99), 297 (4.20). – ^{1}H NMR ($CDCl_3$): δ = 3.65 (s, 3H, CH_3), 6.5 (br. s, 1H, OH), 6.7–7.9 (m, 8H, arom. H). Upon addition of CH_3OD, the signals at δ = 6.5 and 3.65 disappear.

$C_{15}H_{12}N_2O_2$ (252.3) Calcd. C 71.42 H 4.79 N 11.10 O 12.68
Found C 71.49 H 4.78 N 11.03 O 12.58

5,5a,6,11,11a,12-Hexahydro-5,11-dimethylquinoxalino[2,3-b]quinoxaline (**16**): 24 g (0.15 mol) of *N*-methyl-2-nitroaniline (Aldrich, 95%) was reduced with 40 g (0.34 mol) of granulated tin and 180 ml of conc. HCl. The acidic solution of the *N*-methyl-1,2-phenylenediamine was added dropwise under nitrogen with vigorous stirring to a solution of 240 g (6 mol) of NaOH in 1 l of H_2O. About 1.5 l of this solution was distilled under nitrogen whereby the water had to be replenished from time to time. The distillate contained practically all of the amine, to which 14.5 g (0.075 mol) of glyoxal (30% in water) was added with vigorous stirring. After 1–2 min the solution became turbid and crystallization started. After ≈ 12 h the precipitate was filtered off, washed with H_2O and dried; yield 19.15 g (96%) of crude product; m.p. 144–150°C (dec.). Recrystallization (two times from 2-propanol, light-protected and under nitrogen) yielded 11.45 g (57%) of colorless crystals which melted under decomposition, starting at 150°C. – ^{1}H NMR ($CDCl_3$): δ = 3.07 (s, 6H, NCH_3), 3.7 (br. s, 2H, NH), 4.67 (s, 2H, CH), 6.35–6.85 (m, 8H, arom. H). – UV (CH): λ_{max} (lgε) = 307 nm (4.00), 250 (sh) (4.08), 222 (4.78).

$C_{16}H_{18}N_4$ (266.35) Calcd. C 72.15 H 6.81 N 21.04
Found C 72.24 H 6.91 N 21.05

5,5a,6,11,11a,12-Hexahydro-5,6,11,12-tetramethylquinoxalino[2,3-b]quinoxaline (**21**) *and 5,6,11,12-Tetrahydro-5,6,11,12,13,20-hexamethyl-5a,11a-(imino[1,2]benzenoimino)quinoxalino[2,3-b]quinoxaline* (**22**): The preparation of **21** and **22** has been described in ref.[3].

2,2',3,3'-Tetrahydro-3,3'-dimethyl-2,2'-bibenzothiazole (**23**): 50 g of KOH was dissolved under nitrogen in 300 ml of ethanol, 45 g (0.27 mol) of 3-methylbenzothiazolin-2-one[9] was added and the mixture was heated at reflux for 5 h. After cooling, the precipitated potassium salt was decanted and the ethanol evaporated. The oily residue and the potassium salt were dissolved in water, the solution was acidified with HCl (pH ≈ 5), 27 g (0.14 mol) of glyoxal (30% in water) was added and the solution was heated at reflux under nitrogen for 22 h. After cooling, 40.0 g (91%) of crude **23** (m.p. 120–140°C) precipitated. Recrystallization (three times from ethanol) yielded 8.8 g (20%) of colorless crystals (m.p. 155–156°C) and 25 g of less pure material from the mother liquor. – UV (CH): λ_{max} (lgε) = 313 nm (3.95), 260 (sh) (3.91), 231.5 (4.68). – ^{1}H NMR ($CDCl_3$): δ = 3.05 (s, 6H, CH_3), 4.98 (s, 2H, CH), 6.4–7.1 (m, 8H, arom. H). – MS: *m/z* (%) = 300 (3) [M^+], 150 (100), 109 (32).

$C_{16}H_{16}N_2S_2$ (300.5) Calcd. C 63.96 H 5.37 N 9.32 S 21.34
Found C 64.06 H 5.41 N 9.36 S 21.28

5a,6,11a,12-Tetrahydro-6,12-dimethyl[1,4]benzothiazino[3,2-b]-[1,4]benzothiazine (**24**): 1 g of **23** was dissolved in 1.3 l of CH and irradiated (254 nm) for 6 d under nitrogen in a Rayonet reactor. The quartz vessel which contained the solution had to be cleaned every 24 h from a dark precipitate on its walls. The solvent was evaporated and the photoproduct chromatographed on an Al_2O_3 column with CH/diethyl ether (1:1) as eluant. Recrystallization from ethanol yielded 84 mg (8.4%) of colorless crystals, m.p. 166–167°C. – UV (CH): λ_{max} (lgε) = 316 nm (3.96), 232 (4.75). – ^{1}H NMR ($CDCl_3$): δ = 3.02 (s, 6H, CH_3), 5.05 (s, 2H, CH), 6.4–7.1 (m, 8H, arom. H).

$C_{16}H_{16}N_2S_2$ (300.5) Calcd. C 63.96 H 5.37 N 9.32 S 21.34
Found C 64.22 H 5.15 N 9.41 S 21.10

CAS Registry Numbers

1a: 124855-82-9 / **1b**: 124855-83-0 / **1c**: 124855-84-1 / **1d**: 124855-85-2 / **1e**: 124855-86-3 / **1f**: 124855-87-4 / **6**: 124855-93-2 / **9**: 124855-89-6 / **12**: 122433-29-8 / **16**: 124855-90-9 / **20**: 15805-70-6 / **21**: 13784-23-1 / **22**: 124855-94-3 / **23**: 124855-91-0 / **24**: 124855-92-1 / 2-aminophenol: 95-55-6 / glyoxal: 107-22-2 / phenylglyoxal: 1074-12-0 / benzil: 134-81-6 / 1-(2-benzoxazolyl)ethanol: 124855-88-5 / d,l-lactic acid: 598-82-3 / *N*-methyl-2-nitroaniline: 612-28-2 / 3-methylbenzothiazolin-2-one: 2786-62-1 / 2-phenylbenzoxazole: 833-50-1 / benzoxazole: 273-53-0 / 2-methylbenzoxazole: 95-21-6 / 2-(methylamino)phenol: 611-24-5

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[373/89]