placed in a 25-mL volumetric flask and diluted with 20.0 mL of the solvent mixture, and the resulting solution was equilibrated in a constant-temperature bath and diluted to the mark with the solvent mixture. The solution was then transferred to a 50-mL volumetric flask and allowed to equilibrate once more. A 0.1-mL aliquot of sodium hydroxide solution was added and the flask swirled vigorously. The sodium hydroxide was of a known molarity which was chosen to give the desired final concentration, which was at least 10 times the concentration of substrate for reactions run under pseudo-first-order conditions and approximately 2 times the concentration of the substrate for reactions run under second-order conditions. The latter method was used for the undeuterated substrate from 75 °C and up in 30% Me_2SO, 60 °C and up in 40% Me_2SO, and 45 °C and up in 50% Me_2SO.

Immediately after the addition of base and mixing, a portion of the contents of the flask was transferred to a quartz cell in a thermostatically controlled, insulated cell compartment of a Beckman DB-GT spectrophotometer. The temperature was monitored by an iron–constantan thermocouple in the cell compartment. The increase in absorbance vs. time was recorded at the λ_{max} of *p*-(trifluoromethyl)styrene (approximately 260 nm, but dependent on the solvent composition and, to a small extent, the temperature). Rate constants were obtained from the slopes of least-squares fits of the data to the appropriate integrated rate equation. Arrhenius parameters were evaluated from least-squares fits of the data to a plot of ln k *vs.* $1/T$.

Control Experiments. Analysis of the product mixture by GLPC on a 12 ft × 0.125 in. column of 5% SF-96 on Chromosorb W at 50 °C and on a 6 ft × 0.125 in. column of 25% didecyl phthalate on 60–80-mesh firebrick at 150 °C showed no products other than *p*-(trifluoromethyl)styrene and trimethylamine. Solutions of [2-[*p*-(trifluoromethyl)phenyl]ethyl]trimethylammonium iodide in 30%, 35%, 40%, and 50% Me_2SO in the absence of base showed no detectable increase in ultraviolet absorption when kept at 80 °C for up to 24 h.

Registry No. **1d**·I^-, 78698-15-4; **1h**·I^-, 77207-67-1; *p*-(trifluoromethyl)benzyl alcohol, 349-95-1; *p*-(trifluoromethyl)benzoic acid, 455-24-3; [*p*-(trifluoromethyl)phenyl]acetonitrile, 2338-75-2; 2-[*p*-(trifluoromethyl)phenyl]ethylamine, 775-00-8; [*p*-(trifluoromethyl)-phenyl]acetonitrile-α,α-d_2, 78698-16-5; 2-[(*p*-(trifluoromethyl)-phenyl]ethylamine-2,2-d_2, 78698-17-6; [2-[*p*-(trifluoromethyl)-phenyl]ethyl-2,2-d_2]dimethylamine, 78698-18-7; hydroxide ion, 3352-57-6.

Photochemical and Thermal Reactions of Aromatic Schiff Bases

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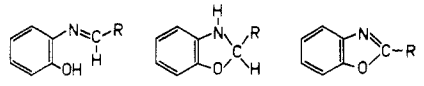
The photochemical and thermal reactions of aromatic Schiff bases (SB) prepared from *o*-aminophenol and aldehydes and from *o*-aminophenol and ketones are compared. All SB's are converted by light into the corresponding benzoxazolines. For the SB's derived from aldehydes, benzoxazoline formation is a prerequisite to convert them by a second photon into benzoxazoles. In some cases oxygen is not required for this second reaction step. SB's derived from ketones are converted into benzoxazoles by the absorption of just one photon, but only in the presence of oxygen and only if the aliphatic residue R_1 of the N=C(R_1R_2) bridge contains at least two carbon atoms. A radical mechanism is proposed for this reaction. Benzoxazine formation is observed in some cases as a thermal side reaction. The photochemical reactions of the latter were also investigated.

The condensation products of *o*-aminophenol and certain aldehydes or ketones (Schiff bases, SB) are readily converted into 2-substituted benzoxazoles if they are illuminated in inert solvents like methylcyclohexane (MCH). The photoconversion of *N*-benzylidene-*o*-aminophenol (**1a**)



1 **2** **3**

(R = Ph; cf. Table I) into 2-phenylbenzoxazole (**3a**) has been investigated by us in some detail.[1] We showed that **1a** is first converted into 2-phenylbenzoxazoline (**2a**) and that a second photon is required to convert **2a** into **3a**. In addition, light-induced trans → cis and thermal- and light-induced cis → trans isomerizations of **1a** take place. Competing with the photodehydrogenation **2a** → **3a** is the thermal and photolytic back-reaction **2a** → **1a**. Due to this back reaction the lifetime of **2a** is about 200 s in the dark at room temperature (cf. Table I). The oxazole **3a** is also formed in degassed solutions of **1a**. In this case molecular hydrogen is evolved, but both the chemical yield and the relative quantum yield are considerably lower than in air-saturated solutions.

Table I. Long-Wavelength Absorption (λ_{max}) of Schiff Base 1, Lifetimes (τ) of the Corresponding Oxazolines 2[a], and Chemical Yields of Formation of the Oxazoles 3[b]

				% chemical yield	
compd	R	λ_{max}, nm	τ, s	air saturated	degassed
1a	C_6H_5	368	200	80	10
b	*o*-C_6H_5OH	357	50	25	20
c	*p*-C_6H_5OH	350	4800	30	dec
d	*o*-$C_6H_5OCH_3$	357	9	30	dec
e	*p*-$C_6H_5OCH_3$	351	15	45	traces
f	α-$C_{10}H_7$	367	600	50	20
g	β-$C_{10}H_7$	363	240	75	60
h	9-anthryl	407	780	80	dec
i	$CH=CHC_6H_5$	366	12	25	dec
k	2-furanyl	365	15	35	25
l	2-thiophenyl	363	45	45	15
m	ferrocenyl	348	10	70	dec
n	$C(CH_3)_3$	315	9000	80	65

[a] At room temperature in air-saturated solutions. [b] The solvent was methylcyclohexane.

The course of the reaction can easily be followed by spectroscopic means because the UV absorption spectra of **1a**–**3a** differ characteristically from each other. Due to resonance interaction between the two phenyl rings across the C=N double bond linkage, **1a** has a broad structureless

(1) Grellmann, K. H.; Tauer, E. *J. Am. Chem. Soc.* **1973**, *95*, 3104–3108.

0022-3263/81/1946-4252$01.25/0

absorption band with a maximum at 368 nm. This long-wavelength band is absent in the benzoxazoline **2a**, and it is therefore possible to excite the SB exclusively by long-wavelength irradiation and to distinguish between the reaction steps **1a** → **2a** and **2a** → **3a**. The oxazoline **2a** is stable at low temperatures, and its absorption spectrum can be measured, e.g., at 210 K, with a conventional spectrophotometer. The absorption spectrum of the oxazole **3a** has four relatively sharp absorption peaks between 315 and 280 nm because of its rather rigid molecular structure.

In part I of this paper we show briefly that the photochemical ring closure reaction **1** → **2** → **3** occurs with a variety of SB's derived from *o*-aminophenol and different aldehydes. In part II we describe some photochemical and thermal reactions of SB's prepared from *o*-aminophenol and ketones, i.e., of compounds in which the hydrogen at the C=N bridge of **1** is replaced by a substituent.

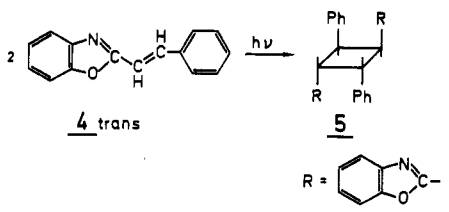
Results

I. Schiff Bases from *o*-Aminophenol and Aldehydes. All reactions were carried out in MCH as solvent. The SB's listed in Table I are all converted into the corresponding benzoxazoles **3** with chemical yields between 25% and 80% if the photoreaction is carried out in air-saturated solutions. In degassed solutions the chemical yields vary from 0% to 65%. The compounds which do not yield oxazoles under anaerobic conditions (**1c,d,h,i,m** in Table I) decompose into unidentified products. Selective excitation into the long-wavelength absorption band (λ_{max} in Table I) converts the SB's into the corresponding oxazolines **2** which decay in the dark with different lifetimes, τ (cf. Table I) back into the starting material.

The SB **1n** is the only compound in Table I with an aliphatic moiety. Attempts to prepare SB's from *o*-aminophenol and aldehydes containing two α-H atoms, e.g., *n*-propion-, *n*-butyr-, or *n*-capronaldehyde, failed. Only dark yellow resinous products were formed. A solution of these products in MCH did not yield oxazoles upon illumination. Isobutyraldehyde with only one α-H atom yields a yellowish oil, and small amounts of 2-isopropylbenzoxazole are formed after illumination of the freshly prepared compound dissolved in MCH. The SB **1n** which contains no α-H atoms is stable for several weeks at room temperature. In contrast to the other derivatives in Table I it is liquid at room temperature.

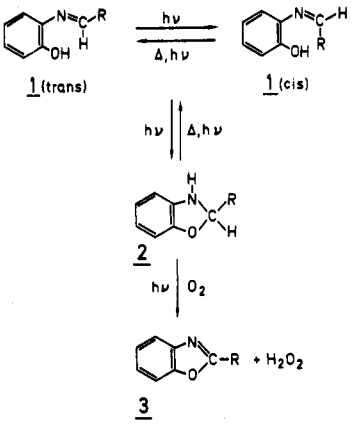
The styrene derivative **1i** yields *cis*- and *trans*-2-styrylbenzoxazole **4** after illumination. The cis/trans ratio depends on the wavelength of the exciting light. Under polychromatic illumination with a medium-pressure mercury lamp about 70% of the oxazole formed is in the cis form. This photostationary cis–trans mixture evolves in solution in a rather complicated fashion because both the SB and the oxazole and presumably also the oxazoline isomerize about the C=C double bond.

It should be mentioned that **4** photodimerizes in the crystalline state. A few experiments carried out at room temperature with crystals of **4** in the trans form showed that the dimer **5** obtained had the structure of α-truxillic

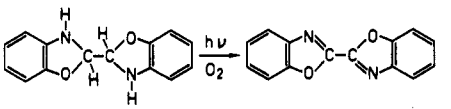


acid. In solution, **5** is cleaved into the monomer **4** upon illumination. It will be interesting to investigate whether this cleavage yields *trans*-**4**, *cis*-**4**, or both.

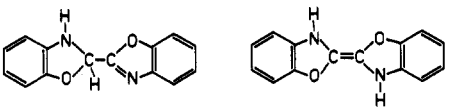
Scheme I



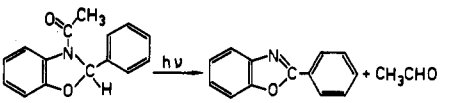
The stable form of the condensation product from *o*-aminophenol and glyoxal is not the corresponding SB but 2,2′-dibenzoxazoline **6**. Solutions of **6** in the presence of oxygen are converted by light into 2,2′-bibenzoxazole (**7**)



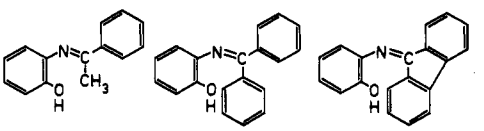
with a chemical yield of 25%. In degassed solution **6** decomposes into unidentified products. We are presently investigating how many photons are required for the reaction **6** → **7** and whether the formation of the oxazoline **8** or the ethylene derivative **9** are intermediates in this reaction sequence.



Another stable oxazoline is 2-phenyl-3-acetylbenzoxazoline (**10**). It yields 2-phenylbenzoxazole (**3a**) and acetaldehyde on illumination in the presence of oxygen and in degassed solution. The chemical yield in air-saturated MCH solution is 70%.



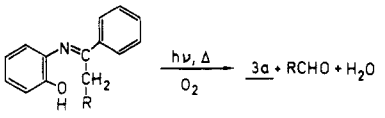
II. Schiff Bases from *o*-Aminophenol and Ketones. Since the photocyclization reactions presented in part I apparently generally follow the route via the oxazolines **2** (see Scheme I), it was of interest to investigate SB's where the hydrogen at the C=N bridge was replaced by another substituent. The simplest examples are the SB's **11** and **12**. Neither yields the corresponding oxazole on



illumination. The same is true for the fluorenone derivative **13** in which the two phenyl rings of **12** are held in a fixed position. All three compounds exhibit the expected

IR spectrum (C=N and OH bands) and the long-wavelength UV absorption band (with maxima at 350, 365, and 430 nm for **11–13**, respectively) typical for SB's. This UV band disappears if the compounds are illuminated at low temperature (210 K), and it reappears if the solutions are allowed to warm up to room temperature. Apparently, the SB's **11–13** are converted into the corresponding oxazolines by illumination but not into oxazoles. The thermodynamically stable form of **11** is presumably the one in which the two phenyl rings are in the trans position.[2] In flash experiments we observed, at 440 nm, the absorption of the cis form. This has a lifetime of 1 s at room temperature. (At 440 nm the trans form does not absorb.)

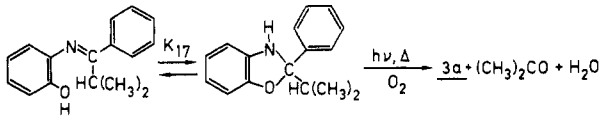
Replacement of the methyl group in the acetophenone derivative **11** by an ethyl, propyl, benzyl, isopropyl, or *tert*-butyl group changes the photochemical properties of the resulting SB's drastically. As in the case of **11–13** and the compounds listed in Table I the azomethine structure of **14–16** is the stable configuration at room temperature.



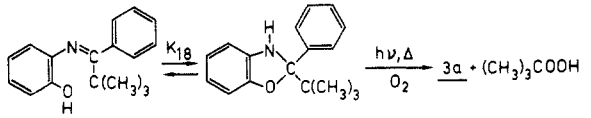
14: R = CH_3; **15**: R = C_2H_5; **16**: R = C_6H_5

This is shown by the IR spectra of these compounds in the crystalline state. Likewise, the UV absorption spectra of **14–16** show the characteristic long-wavelength absorption with maxima at 347, 345, and 353 nm, respectively. At low temperature (200 K) where other photoreactions are suppressed the tautomeric oxazolines can be prepared by long wavelength excitation. In the dark they convert back to the SB's if the solutions are allowed to warm up to room temperature.

In contrast to **14–16** the IR and UV absorption spectra show that crystals of **18** have the oxazoline structure **18b**.



17a **17b**



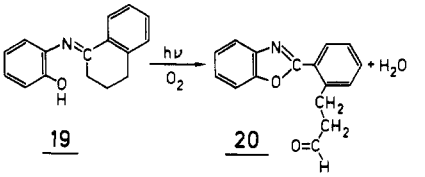
18a **18b**

A freshly prepared solution of **18** shows no long-wavelength absorption band. At 295 K a shoulder develops at 330 nm with a "half-life" of about 3 h due to the absorption of **18a** which is in thermal equilibrium with **18b**. In a freshly prepared solution of **17** a long-wavelength absorption with maximum at 330 nm is already present. If one assumes that the extinction coefficient of this band has the same value as that of **23** (see below) and that the extinction coefficients of **17b** and **18b** are equal, one can estimate that in solution at room temperature the equilibrium constants K = [a]/[b] are $K_{17} \approx 0.5$ and $K_{18} \approx 0.3$.

In contrast to **11–13**, the five derivatives **14–18** are converted into 2-phenylbenzoxazole (**3a**) by light, but only in the presence of oxygen. The alkyl residue is oxidatively cleaved as acetaldehyde from **14**, propionaldehyde from **15**, benzaldehyde from **16**, acetone from **17**, and *tert*-butylhydroperoxide from **18**. Irradiation in the long-wavelength absorption band of the SB's **14–18** leads in the presence of oxygen to the formation of **3a** at room temperature. Since the corresponding oxazolines do not absorb at these wavelengths, it follows that **3a** is formed directly from the SB's. In agreement with this, no induction period is found if illumination experiments with polychromatic light are carried out during which the formation of **3a** is measured as a function of illumination time.

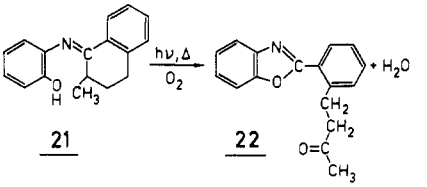
If one keeps air-saturated solutions of **14–18** for 1–2 weeks in the dark, 2-phenylbenzoxazole (**3a**) is also formed. Acetaldehyde, propionaldehyde, benzaldehyde, acetone, and *tert*-butyl hydroperoxide are again the byproducts. Degassed solutions, however, are stable in the dark. The chemical yield of the above light and dark reactions is 40–60%.

To further investigate the remarkable difference in reactivity between **11** and **14–18**, we synthesized the SB **19** from tetralone and *o*-aminophenol. In this compound the propyl group is linked to the benzylidene moiety. In the dark only traces of **20** are formed from an air-saturated solution of **19**, in contrast to the open-chain analogue **15**. Illumination of **19** at long wavelengths (**19** has an absorption maximum at 345 nm) yields **20** in only about 10%



19 **20**

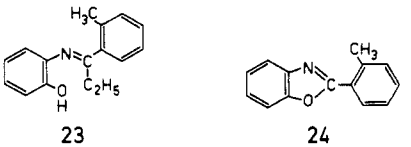
chemical yield. (The estimation of this yield is based on the assumption that the extinction coefficients of **22** and **20** are equal.) We were unsuccessful in our attempts to isolate **20** from solution because the substance decomposes, presumably by reacting with the starting material **19**, yielding tetralone and an SB with an aliphatic moiety. In part I it has been mentioned already that the condensation products of *o*-aminophenol and aliphatic aldehydes are unstable and tend to polymerize. Therefore, we synthesized the SB **21** in which the tetralone ring contains a methyl group. This compound is readily converted into the benzoxazole **22** by irradiation and in the dark. In



21 **22**

contrast to **20**, the oxazole **22** is a stable compound and can easily be isolated because it contains instead of an aldehyde group a keto group which does not react with **21** at room temperature. The chemical yield of the light-induced reaction is 80% if one excites **21** with-long wavelength light around 350 nm. Under polychromatic excitation the yield drops to 20% because the product **22** is photochemically unstable. The chemical yield of the dark reaction is 90%.

Introduction of an *o*-methyl group into the benzylidene moiety of **14** yields SB **23**. Due to this *o*-methyl group



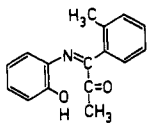
23 **24**

the resonance across the C=N double bond linkage is

(2) Fischer, E.; Frei, Y. *J. Chem. Phys.* **1957**, *27*, 808.

reduced by steric hindrance which causes a blue shift of the long-wavelength absorption maximum from 345 (SB 14) to 325 nm. A similar shift is observed with 17 and 18 and also if the ethyl group of 23 is replaced by a methyl group. (In the latter case the resulting SB is, however, nonreactive like 11. The *p*-tolyl analogue is also nonreactive but has an absorption maximum at 345 nm.) Air-saturated solutions of 23 are, similar to those of 14, converted by light into 2-*o*-tolylbenzoxazole (24) with 20% chemical yield. In the dark, however, the properties of 23 are entirely different from those of 14 because 2-methyl-2-hydroxy-3-*o*-tolylbenzoxazine (25) is formed with 90%

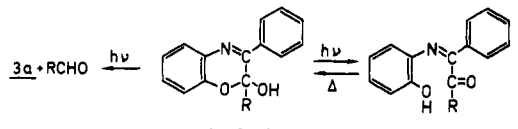
25



26

chemical yield instead of 24. The benzoxazine is a stable compound with an absorption peak at 290 nm and a shoulder at 315 nm. In degassed as in air-saturated solutions, 25 is converted by light into 2-*o*-tolylbenzoxazole (24) and acetaldehyde. In addition, one observes during illumination the formation of an unstable compound which has a broad absorption band with a maximum at 365 nm. It has a lifetime of 1200 s at room temperature and decays entirely back into the starting material. We therefore assume that this compound is the SB 26. Due to its limited lifetime the photostationary concentration of 26 is lower at lower intensities of the actinic light. As a consequence, more oxazole is produced, if the light intensity is decreased by a certain factor with neutral-density filters and the illumination time prolonged by the same factor. This observation also indicates that 26 is not photoreactive, i.e., 24 is produced only from 25. A quantitative study of these reactions is in progress.

Since the introduction of an *o*-methyl group into the benzylidene moiety of 14 had such a drastic effect on the dark reaction and since the photoreaction of 25 is rather interesting in itself, it seemed worthwhile to compare the properties of 25 with those of the oxazines 27 and 28 which



27: R = CH_3 29: R = CH_3

28: R = C_6H_5 30: R = C_6H_5

do not contain an *o*-methyl group. Both compounds behave photochemically like 25, i.e., the SB's 29 and 30, respectively, and benzoxazole 3a together with the corresponding aldehydes are formed in degassed as well as in air-saturated solutions. The lifetime of SB 29 at room temperature is about 50 s and that of 30 about 1000 s. Oxazines 27 and 28 are stable compounds which could easily be detected if they were formed in dark reactions from 14 or 16, respectively. Only traces of 27 were found in a solution of 14 after it was allowed to stand in the dark, while during the same time 50% of 3a was formed as described above. Under the same conditions about 10% 28 and 60% 3a were formed from a solution of 16.

Discussion

The common property of all SB's described in this paper is their conversion into the tautomeric benzoxazolines. Due to the long-wavelength absorption band of the SB's it is easy to observe this reaction step, to avoid exposure of photoproducts, and to determine the lifetime τ of the benzoxazolines by measuring the rate at which the SB absorption reappears in the dark. The variation of τ caused by minor changes in molecular structure (cf. Table I) is amazingly high: the lifetimes vary between 10 and 9000 s. Similar variations were observed with dihydrocarbazoles formed from diphenylamines,[3] dihydroindoles from enamines,[4] and dihydrophenanthrenes from diarylethylenes.[5]

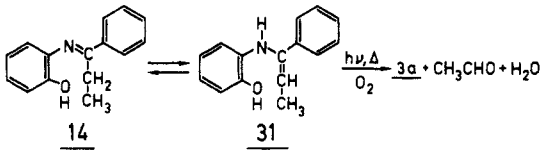
Benzoxazolines with a C–H bond in the heterocycle (Scheme I) undergo no dark reaction other than the ring-opening 2 → 1 back to the SB's; i.e., their lifetime τ is entirely determined by this reaction. Long-wavelength irradiation (where the benzoxazolines 2 do not absorb) leads, therefore, to a steady-state mixture of 1 and 2 the composition of which at a given absorbed light intensity and temperature is determined by τ. Parallel to the oxazoline formation 1 → 2, trans → cis isomerization about the C=N double bond of 1 takes place. The photostationary state of the trans–cis mixture is reached more rapidly than that of the SB–oxazoline mixture because of the short lifetime of the cis form of the SB. It is not possible to excite the trans or the cis form of 1 exclusively because their absorption spectra differ only slightly from each other. Therefore, it would be very difficult to determine whether the ring closure *cis*-1 → 2 or *trans*-1 → 2 has the higher quantum yield. Since the residue, R, of 1 is twisted out of the plane of the aminophenol ring in both isomers, their reactivity may be rather similar.

Once a benzoxazoline 2 is formed a second photon is required to convert it into a benzoxazole 3. The quantum yield of such a reaction is reduced by the competing photolytic step 2 → 1. It is easy to prove that long-wavelength irradiation of 1 does not lead to the formation of 3. However, because both 1 and 2 absorb at shorter wavelength it is quite difficult to determine quantitatively the extent of a direct conversion, 1 → 3, which is quite possible under short-wavelength irradiation. Illumination of a solution of 1a with 254-nm light alone and simultaneous excitation of an identical solution with 254- and 366-nm light for the same length of time yields more benzoxazole 3a in the latter case, and we estimate that as an upper limit 10% of 3a is formed directly from 1a by 254-nm light, the main fraction, however, via 2a.

Quite different are the reaction pathways of the SB's derived from *o*-aminophenol and ketones which are described in part II of this paper. Ring closure, yielding 2-R′-2-phenylbenzoxazolines, also occurs. However, in contrast to the SB's of part I this step is not a prerequisite for the formation of 2-R-benzoxazoles, as the long-wavelength illumination experiments have shown. Another, equally significant, difference is their reactivity in the dark. Both the thermal and the photochemical reactions occur only if oxygen is present in the solution, whereas some of the SB's of part I react also under anaerobic conditions.

The nonreactivity of 11 on the one hand and the facile conversion of 14 into 3a, acetaldehyde, and water on the other is surprising. It led us first to the assumption that the enamine 31 is a precursor of 3a. Similar photooxygenations were observed, e.g., by Foote[6] et al. and by Huber.[7] However, SB 18, which contains a *tert*-butyl group, is converted into 3a with about the same chemical

(3) Förster, E. W. Ph.D. Thesis, Stuttgart, 1971.
(4) Grellmann, K. H.; Kühnle, W.; Wolff, T. *Z. Phys. Chem. (Wiesbaden)* **1976**, *101*, 295–306.
(5) Wismonski-Knittel, T.; Fischer, G.; Fischer, E. *J. Chem. Soc., Perkin Trans. 2* **1974**, 1931.
(6) Foote, C. S.; Wei Pin Lin, J. *Tetrahedron Lett.* **1968**, 3267–3270.
(7) Huber, E. J. *Tetrahedron Lett.* **1968**, 3271–3272.

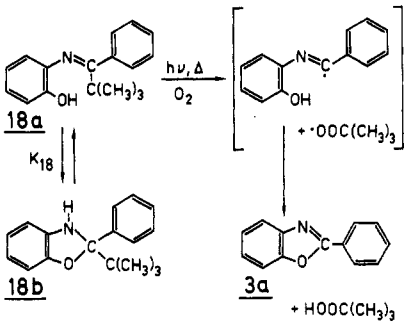


14 31

yield as **14** although enamine formation is, of course, not possible in this case. Oxygen is required for the light-induced and thermally induced conversions of the SB's **14–18** into **3a** and the corresponding aldehydes, ketones, or peroxides. Therefore, we assume as a common first reaction step the attack of oxygen on the α-carbon atom of the aliphatic chain to yield two radicals (cf. Schemes II and III) which react with each other to the final products. In the case of the *tert*-butyl compound **18** (Scheme II) it is again quite easy to show by selective long-wavelength excitation that the open-chain form **18a** is photoreactive, as indicated in Scheme II. However, because of the equilibrium between **18a** and **18b** the question remains open whether **18b** is also attacked by oxygen.

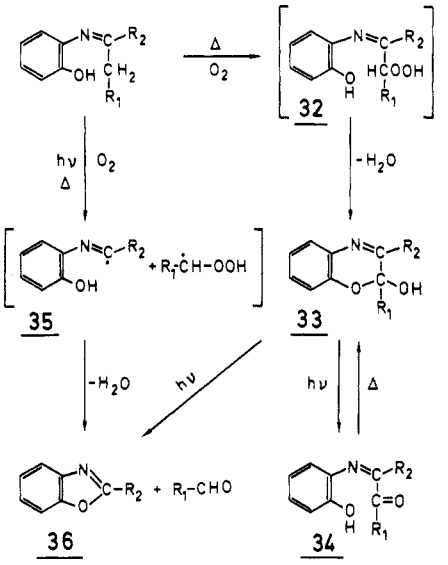
Besides the α-carbon bond cleavage, another dark-reaction pathway has to be assumed which leads to benzoxazine formation. The latter is the predominant thermal reaction product in case of SB **23**. We therefore propose the intermediate formation of the hydroperoxide **32** (Scheme III), which is of course not possible in the case of SB **18a** (Scheme II). Compound **32** decays into the stable oxazine **33**. The other thermal reaction branch in Scheme III (formation of oxazole **36** via intermediate **35**) is quite similar to the one in Scheme II. The branching into these two reaction pathways is influenced by rather minute changes in molecular structure: SB **14** (with a phenyl moiety) reacts practically completely via carbon bond cleavage to yield oxazole **36** and SB **23** (with an *o*-tolyl moiety) predominantly via the other branch, yielding oxazine **33**. Steric hindrance due to the *o*-methyl group in SB **23** causes a blue shift of the long-wavelength absorption from 345 (SB **14**) to 325 nm. This steric hindrance may also be the reason for the difference in reactivity.

Scheme II



18a 18b 3a

Scheme III



35 32 33 36 34

Experimental Section

Methylcyclohexane (Fluka purum) was chromatographed on a Silica–aluminum oxide column. UV spectra were recorded on a Cary 17, IR spectra on a Perkin-Elmer 257, and mass spectra on a Varian MAT CH 7 at 70 eV. Elemental analysis was carried out by the Microanalytical Laboratory Beller.

Photolysis was carried out with a 60-W medium-pressure mercury lamp (Osram Hg 3) in rectangular quartz cells of 10 mm × 10 mm cross section. About 10^{-4} M solutions were either air-saturated or degassed on a high-vacuum line by the freeze–pump–thaw technique. Photoproducts were identified and chemical yields determined by comparing the absorption spectra of authentic samples with the spectra of the illuminated solutions. The accuracy of the rather simple method by which the chemical yields were determined is relatively high (±5%) because the SB's have broad, unstructured absorption maxima, whereas the corresponding oxazoles are characterized by several sharp absorption peaks. Cooling of the cells was achieved by means of the copper block technique.[23]

Some of the photoproducts were prepared in gram amounts by immersing a 125-W high-pressure Osram mercury lamp into a solution of 1–2 g of starting material in 250 mL of MCH. During the illumination the solution was stirred and water cooled. After purification the photoproducts showed no mixture melting point depression with authentic samples. The following compounds were prepared this way: **3a** from **1a** and **10**; **3b** from **1b**; **22** from **21** (no comparison with authentic sample possible); **7** from **6**; **24** from **23**.

Aldehydes and ketones were identified by preparing the 2,4-dinitrophenylhydrazone derivatives. For this purpose a stream of air was first passed through the reaction mixture and then through a solution of 0.4 g of 2,4-dinitrophenylhydrazine in 2 mL of concentrtated H_2SO_4, 3 mL of H_2O, and 10 mL of ethanol for about 2 h and the precipitate recrystallized from ethanol. *tert*-Butyl hydroperoxide was extracted from the MCH solution with water and identified by potentiometric titration.

All melting points are uncorrected.

Schiff Bases. In general, the SB's in Table I were prepared by refluxing 0.1 mol of *o*-aminophenol and 0.1 mol of aldehyde in 100 mL ethanol. After the mixtures cooled, the SB's precipitated and were recrystallized from dry ethanol.

***N*-Benzylidene-*o*-aminophenol (1a)**, mp 94 °C (lit.[8] mp 95 °C).

***N*-(*o*-Hydroxybenzylidene)-*o*-aminophenol (1b)**, mp 190 °C (lit.[8] mp 185 °C).

***N*-(*p*-Hydroxybenzylidene)-*o*-aminophenol (1c)**, mp 154 °C (lit.[9] mp 152 °C).

***N*-(*o*-Methoxybenzylidene)-*o*-aminophenol (1d)**: dark yellow flakes from ethanol; mp 109 °C. Anal. Calcd for $C_{14}H_{13}NO_2$: C, 74.01; H, 5.73; N, 6.17. Found: C, 74.08; H, 5.61; N, 6.06.

***N*-(*p*-Methoxybenzylidene)-*o*-aminophenol (1e)**: dark yellow flakes from ethanol; mp 91–93 °C. Anal. Calcd for $C_{14}H_{13}NO_2$: C, 74.01; H, 5.73; N, 6.17. Found: C, 74.04; H, 5.69; N, 6.20.

***N*-(1-Naphthylmethylene)-*o*-aminophenol (1f)**, mp 76 °C (lit.[10] mp 76–77 °C).

***N*-(2-Naphthylmethylene)-*o*-aminophenol (1g)**: green-yellow crystals from ethanol; mp 88 °C. Anal. Calcd for $C_{17}H_{13}NO$: C, 82.59; H, 5.26; N, 5.67. Found: C, 82.59; H, 5.29; N, 5.75.

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***N*-(9-Anthrylmethylene)-*o*-aminophenol (1h)**, mp 122–124 °C (lit.[10] mp 118 °C).

***N*-(3-Phenyl-2-propenylidene)-*o*-aminophenol (1i)**, mp 92 °C (lit.[11] mp 90 °C).

***N*-(2-Furanylmethylene)-*o*-aminophenol (1k)**, mp 68 °C (lit.[10] mp 69–70 °C).

***N*-(2-Thienylmethylene)-*o*-aminophenol (1l)**, mp 83 °C (lit.[12] mp 80–81 °C).

***N*-(Ferrocenylmethylene)-*o*-aminophenol (1m).** A 23.6-g (0.11 mol) sample of ferrocenealdehyde and 10.9 g (0.1 mol) of *o*-aminophenol in 150 mL toluene were boiled in a Dean–Stark trap until 0.1 mol of H_2O was separated. Part of the crude precipitate (70% yield) was purified on a silica gel column (elution with cyclohexane–ether, 1:1 by volume) and afforded brown-violet crystals, mp 100 °C (lit.[10] mp 71 °C). Anal. Calcd for $C_{17}H_{15}FeNO$: C, 66.88; H, 4.92; N, 4.59. Found: C, 66.62; H, 4.85; N, 4.51.

***N*-(2,2-Dimethylpropylidene)-*o*-aminophenol (1n).** A 28.5-g (0.33 mol) sample of pivaldehyde (2,2-dimethylpropanal) and 32.7 g (0.3 mol) *o*-aminophenol in 150 mL cyclopentane were boiled in a Dean–Stark trap until 0.3 mol of H_2O was separated. Solvents with a higher boiling point reduce the yield. After evaporation of the solvent and fractional distillation a colorless liquid with a boiling point of 100 °C (1 mm) was obtained in 70% yield. Anal. Calcd for $C_{11}H_{15}NO$: C, 74.6; H, 8.47; N, 7.91. Found: C, 74.71; H, 8.51; N, 7.85.

2,2′-Benzoxazoline (6), mp 227 °C (lit.[20] mp 210 °C).

2-Phenyl-3-acetylbenzoxazoline (10), mp 100 °C (lit.[21] mp 98.5 °C).

Schiff bases from *o*-aminophenol and ketones were prepared by boiling 0.2 mol of *o*-aminophenol and 0.22 mol of ketone in 150 mL of toluene under nitrogen atmosphere until 0.2 mol of H_2O was separated in a Dean–Stark trap. The solvent was partly removed. After the mixtures cooled, the SB's crystallized and were purified by recrystallization from dry methanol or toluene under nitrogen. The crude product yield is generally about 90%. The compounds tend to hydrolyze if they are not handled under exclusion of H_2O. The IR spectra of the compounds are characterized by a very broad OH band around 3100 cm^{-1} and a C=N band between 1600 and 1650 cm^{-1}. The UV spectra show a long-wavelength absorption band with a maximum around 350 nm. In cases where the corresponding oxazolines are the stable configuration, the OH and C=N bands are missing, and an N—H band between 3300 and 3500 cm^{-1} is observed. The UV absorption is shifted in those cases to about 290 nm.

***N*-(1-Phenylethylene)-*o*-aminophenol (11)**: dark yellow crystals; mp 88 °C; UV (MCH) λ_{max} 350 nm (ϵ 4200), 250 (15 300). Anal. Calcd for $C_{14}H_{13}NO$: C, 79.62; H, 6.16; N, 6.64. Found: C, 79.15; H, 6.22; N, 6.75.

***N*-(Diphenylmethylene)-*o*-aminophenol (12)**: yellow crystals; mp 159 °C (lit.[13] mp 157 °C); UV (MCH) λ_{max} 366 nm (ϵ 6500), 275 (sh, 10 200) 251 (16 600).

***N*-(Fluoren-9-ylidene)-*o*-aminophenol (13)**: bright yellow crystals; mp 193–195 °C; UV (MCH) λ_{max} 430 nm (ϵ 4700), 298 (sh 8800), 288 (9820), 258 (41 900). Anal. Calcd for $C_{19}H_{15}NO$: C, 84.13; H, 4.80; N, 5.17. Found: C, 83.99; H, 4.89; N, 5.19.

***N*-(1-Phenylpropylidene)-*o*-aminophenol (14)**: dark yellow crystals; mp 78–80 °C; UV (MCH) λ_{max} 347 nm (ϵ 2500), 285 (sh 4100), 247 (10 900). Anal. Calcd for $C_{15}H_{15}NO$: C, 80.00, H, 6.67; N, 6.22. Found: C, 80.04; H, 6.57; N, 6.33.

***N*-(1-Phenylbutylidene)-*o*-aminophenol (15)**: dark yellow crystals; mp 70–71 °C; UV (MCH) λ_{max} 345 nm (ϵ 3400) 250 (13 900). Anal. Calcd for $C_{16}H_{17}NO$: C, 80.33, H, 7.11; N, 5.86. Found: C, 79.99; H, 7.00; N, 5.9.

***N*-(1,2-Diphenylethylidene)-*o*-aminophenol (16)**: dark yellow crystals; mp 88–90 °C; UV (MCH) λ_{max} 353 nm (ϵ 3600), 248 (12 800). Anal. Calcd for $C_{20}H_{17}NO$: C, 83.62; H, 5.92; N, 4.88. Found: C, 83.68; H, 5.92; N, 4.85.

***N*-(2-Methyl-1-phenylpropylidene)-*o*-aminophenol (17a) and 2-isopropyl-2-phenylbenzoxazoline (17b)**: yellowish oil (impure mixture of **17a** and **17b**); UV (MCH) λ_{max} 325 nm (sh), 293, 235 (sh). Anal. Calcd for $C_{16}H_{17}NO$: C, 80.33; H, 7.11; N, 5.86. Found: C, 78.58; H, 6.78; N, 5.97.

2-*tert*-Butyl-2-phenylbenzoxazoline (18b): colorless crystals; mp 97 °C; UV (MCH) λ_{max} 294 nm (ϵ 4700), 240 (sh, 3000). Anal. Calcd for $C_{17}H_{19}NO$: C, 80.63; H, 7.51; N, 5.53. Found: C, 80.81; H, 7.43; N, 5.66.

***N*-(3,4-Dihydro-1(2*H*)-naphthylidene)-*o*-aminophenol (19)**: light yellow crystals; mp 140 °C; UV (MCH) λ_{max} 357 nm (5600), 259 (16 600). Anal. Calcd for $C_{16}H_{15}NO$: C, 81.01; H, 6.33; N, 5.91. Found: C, 81.02; H, 6.59; N, 5.8.

***N*-(3,4-Dihydro-2-methyl-1(2*H*)-naphthylidene)-*o*-aminophenol (21)**: light yellow crystals; mp 131–133 °C; UV (MCH) λ_{max} 354 nm (ϵ 3700), 256 (16 100). Anal. Calcd for $C_{17}H_{17}NO$: C, 81.27; H, 6.77; N, 5.58. Found: C, 81.32; H, 6.83; N, 5.66.

***N*-(1-*o*-Tolylpropylidene)-*o*-aminophenol (23)**: light yellowish, almost colorless crystals; mp 48 °C; UV (MCH) λ_{max} 323 nm (ϵ 3900). Anal. Calcd for $C_{16}H_{17}NO$: C, 80.33; H, 7.11; N, 5.86. Found: C, 80.15; H, 7.14; N, 5.96.

2-[2-(γ-Oxybutyl)phenyl]benzoxazole (22). A 5-g sample of *N*-(3,4-dihydro-2-methyl-1(2*H*)-naphthylidene)-*o*-aminophenol (**21**) was suspended in 500 mL of dry MCH in the dark for 12 days, and dry air was bubbled through. Recrystallization of the reaction product from MCH gave colorless crystals: mp 90–91 °C; UV (MCH) λ_{max} 316 nm (ϵ 11 500), 308 (sh 14 700), (23 100), (2o 100), 295 (22 200), 290 (22 000). Anal. Calcd for $C_{17}H_{15}NO_2$: C, 76.98; H, 5.66; N, 5.28; O, 12.10. Found: C, 77.18; H, 5.79; N, 5.31; O, 12.00.

2-Methyl-3-*o*-tolyl-2*H*-1,4-benzoxazin-2-ol (25). A 5-g sample of *N*-(1-*o*-Tolyl-propylidene)-*o*-aminophenol (**23**) was suspended in 500 mL dry MCH in the dark for 2 days, and dry air was bubbled through. Recrystallization of the reaction product from MCH gave colorless crystals: mp 140–142 °C; UV (MCH) λ_{max} 310 nm (sh ϵ 4900), 267 (9500). Anal. Calcd for $C_{16}H_{15}NO_2$: C, 75.89; H, 5.93; N, 5.53; O, 12.65. Found: C, 76.01; H, 5.99; N, 5.59; O, 12.51.

2-Methyl-3-phenyl-2*H*-1,4-benzoxazin-2-ol (27). A 21.8-g (0.2 mol) sample of *o*-aminophenol and 33 g (0.22 mol) 1-phenylpropane-1,2-dione were boiled in 150 mL of toluene on a Dean–Stark trap until 0.2 mol of H_2O was separated. The crude crystalline material was recrystallized from toluene: light yellow crystals; mp 120–122 °C; UV λ_{max} 335 nm (sh, ϵ 6700), 284 (13 600). Anal. Calcd for $C_{15}H_{13}NO_2$: 75.31; H, 5.48; N, 5.85; O, 13.37. Found: C, 75.37; H, 5.56; N, 5.78; O, 13.14.

2,3-Diphenyl-2*H*-1,4-benzoxazin-2-ol (28) was synthesized and purified like **27** from *o*-aminophenol and benzil: light yellow crystals; mp 147 °C; UV λ_{max} 335 nm (sh ϵ 7000), 285 (13 900). Anal. Calcd for $C_{20}H_{15}NO_2$: C, 79.73; H, 4.98; N, 4.65; O, 10.63. Found: C, 79.65; H, 5.15; N, 4.55; O, 10.66.

The 2-R-benzoxazoles **3** with the residues R listed in Table I were (with the exception of **3n**) prepared from the corresponding Schiff bases **1** by oxidation with lead tetraacetate in glacial acetic acid by the procedure of Stephens and Bower.[11,14] The same method was employed to prepare **4** from **1i** and **7** from **6**.

2-Phenylbenzoxazole (3a), mp 105 °C (lit. mp[14] 102 °C).

2-(*o*-Hydroxyphenyl)benzoxazole (3b), mp 127 °C (lit.[15] mp 122–123 °C).

2-(*p*-Hydroxyphenyl)benzoxazole (3c): colorless crystals after vacuum sublimation and recrystallization from ethanol; mp 257–260 °C; yield after purification 18%. Anal. Calcd for $C_{13}H_9NO_2$: C, 73.90; H, 4.26; N, 6.64. Found: C, 73.88; H, 4.32; N, 6.64.

2-(*o*-Methoxyphenyl)benzoxazole (3d): colorless crystals after recrystallization from ethanol–water and vacuum sublimation; mp 57 °C; yield after purification 10%. Anal. Calcd for $C_{14}H_{11}NO_2$: C, 74.7; H, 4.89; N, 6.22. Found: C, 74.48; H, 4.98; N, 6.14.

2-(*p*-Methoxyphenyl)benzoxazole (3e), mp 101 °C (lit.[15] mp 101 °C).

2-(α-Naphthyl)benzoxazole (3f), mp 104 °C (lit.[16] mp 104–105 °C).

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2-(β-Naphthyl)benzoxazole (3g), mp 112 °C (lit.[16] mp 113–115 °C).

2-(9-Anthryl)benzoxazole (3h): dark yellow crystals after recrystallization from 2-propanol; mp 169–172 °C. Anal. Calcd for $C_{21}H_{13}NO$: C, 85.42; H, 4.41; N, 4.75. Found: C, 85.38; H, 4.38; N, 4.64.

***trans*-2-Styrylbenzoxazole (4)**, mp 84 °C (lit.[14] mp 81 °C).

***cis*-2-Styrylbenzoxazole (4).** Into a solution of 20 g of *trans*-2-strylylbenzoxazole in 2 L of methanol was immersed a 125-W medium-pressure Hg lamp, and the solution was illuminated through Pyrex until the photostationary state was reached (control by UV spectra of aliquots). After evaporation of the solvent, the trans–cis mixture was fractionated by distillation. The first fraction [bp 140 °C (1 mm)] was the cis form: yield about 30% (6g); light yellow, almost colorless crystals; mp 35 °C; mol wt calcd 221, found 231. Anal. Calcd for $C_{15}H_{11}NO$: C, 81.45; H, 4.98; N, 6.33; O, 7.14. Found: C, 81.79; H, 4.93; N, 6.23; O, 6.95.

2-(2-Furanyl)benzoxazole (3k), mp 89–90 °C (lit. mp 82–84 °C[14] 86–86.5 °C[15]).

2-(2-Thiophenyl)benzoxazole (3l), mp 107 °C (lit.[17] mp 104.5 °C).

2-Ferrocenylbenzoxazole (3m): orange crystals after recrystallization from ethanol and vacuum sublimation; mp 150 °C. Anal. Calcd for $C_{17}H_{13}FeNO$: C, 67.33; H, 4.29; N, 4.62. Found: C, 67.34; H, 4.41; N, 4.67.

2-*tert*-Butylbenzoxazole (3n) was prepared by the procedure of Skraup[18] from *o*-aminophenol and pivalic acid (2,2-dimethylpropanoic acid): colorless liquid; bp 222–226 °C (lit.[18] bp 226 °C).

2-*o*-Tolylbenzoxazole (24), mp 69 °C (lit.[22] mp 69 °C).

1,3-Diphenyl-2,4-bis(2-benzoxazolyl)cyclobutane (5). A 10-g sample of *trans*-2-styrylbenzoxazole (4) was horizontally and evenly distributed in Pyrex tubing of 100-mm i.d., and 500-mm length and in a horizontally located Rayonet-Reactor under slow rotation (4 turns/min) and illuminated with 300-nm light for 6 days. The unreacted styrylbenzoxazole was removed with 100 mL of ethanol and the residue recrystallized from acetone: yield 2.2 g (22%); colorless crystals; mp 248 °C; mol wt ($CHCl_3$) calcd 442, found 454; mass spectrum, main mass *m/e* 221 (styrylbenzoxazole), parent peak (*m/e* 442) only traces, no signal at *m/e* 180 (stilbene), no signal at *m/e* 262 (1,2-dibenzoxazolylethylene). Anal. Calcd for $C_{30}H_{22}N_2O_2$: C, 81.45; H, 4.98; N, 6.33; O, 7.24. Found: C, 81.52; H, 4.88; N, 6.28; O, 7.12.

The main mass (styrylbenzoxazole) indicates that **5** has the structure of a truxillic acid because it is highly improbable that a compound with a truxinic acid structure would cleave only into styrylbenzoxazole and not into stilbene plus 1,2-dibenzoxazolylethylene.

Furthermore, if **5** is hydrolyzed for 2 h with boiling diluted H_2SO_4 (10%), epitruxillic acid (mp 285 °C) is formed. Since either the α- or the ε-truxillic acid derivative is the most probable configuration of the photodimer derived from **4** in its trans form and since α-truxillic acid but not ε-truxillic acid yields epi-truxillic acid in boiling H_2SO_4[19] we conclude that **5** has the structure of an α-truxillic acid derivative.

2,2′-Bibenzoxazole (7), mp 262 °C (lit.[20] mp 256 °C).

Acknowledgment. We thank Miss A. Renneberg for technical assistance.

Registry No. 1a, 3230-45-3; **1b**, 1761-56-4; **1c**, 17065-03-1; **1d**, 6136-58-9; **1e**, 3117-67-7; **1f**, 5932-25-2; **1g**, 78685-68-4; **1h**, 6076-01-3; **1i**, 54638-91-4; **1k**, 6078-02-0; **1l**, 1435-04-7; **1m**, 12126-35-1; **1n**, 70299-35-3; **3a**, 833-50-1; **3b**, 835-64-3; **3c**, 3315-19-3; **3d**, 13459-17-1; **3e**, 838-34-6; **3f**, 3164-18-9; **3g**, 14625-56-0; **3h**, 78685-69-5; **3k**, 881-60-7; **3l**, 23999-63-5; **3m**, 34801-92-8; **3n**, 54696-03-6; *cis*-**4**, 78685-70-8; *trans*-**4**, 59066-62-5; **5**, 78685-71-9; **6**, 26903-08-2; **7**, 7210-07-3; **10**, 78685-72-0; **11**, 20768-44-9; **12**, 75729-97-4; **13**, 33771-63-0; **14**, 78685-73-1; **15**, 78685-74-2; **16**, 33771-65-2; **17a**, 78685-75-3; **17b**, 78685-76-4; **18b**, 78685-77-5; **19**, 78685-78-6; **20**, 78685-79-7; **21**, 78685-80-0; **22**, 78685-81-1; **23**, 78685-82-2; **24**, 32959-60-7; **25**, 78685-83-3; **27**, 78685-84-4; **28**, 78685-85-5.

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Photoreactivity of 2- and 3-Substituted Benzo[*b*]thiophene 1-Oxides in Solution

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The photochemical behavior of various benzo[*b*]thiophene sulfoxides (3-methyl, 3-phenyl, 2-methyl, 2-phenyl, 2,3-dimethyl, 2-chloro, 2-bromo, 3-chloro, 3-bromo) has been studied in benzene as solvent. The bromo and chloro derivatives gave no identifiable products. The 3-methyl and 3-phenyl compounds gave three head to head anti photodimers which differ only by the stereochemistry of the S–O bond. The kinetics of the photodimerization of 3-MeBTO was studied as a function of the concentration of substrate, triplet quencher, and triplet sensitizer. A monomeric excited triplet is the proposed precursor of the hth dimer. The 2-methyl derivative led to a photoreduction giving the corresponding sulfide probably through an excited triplet. The 2-phenyl derivative gave a mixture of the photodimer hth and the corresponding sulfide. The behavior of the sulfoxides in these series is different from that of the corresponding sulfones which lead to a mixture of hth and htt dimers for the 2-substituted compounds and to the hth dimer for the 3-substituted ones.

The photochemical behavior of sulfoxides can be classified in different categories according to the type of chemical reaction observed: epimerization of the sulfoxide group;[1-3] ring contraction with loss of oxygen as in case of 2,2-dimethylthiachroman 1-oxide[4] and of analogous cyclic sulfoxides;[5] loss of a β-hydrogen atom leading to a ring

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