Chemistry of Nitrosoimines. II.⁽¹⁾ Photolysis of 2-Nitrosoimino-2,3-dihydrothiazoles

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(Received November 30, 1971)

Irradiation of 3-substituted 2-nitrosoimino-2,3-dihydrobenzothiazoles (I) with a medium pressure mercury lamp gave bis[*o*-(*N*-substituted cyanamino)phenyl] disulfides (III) in high yields. Irradiation of 4,5-diphenyl-2-nitrosoimino-2,3-dihydrothiazole (VI) gave bis[(2-phenyl-2-*N*-phenylcyanamino)vinyl] disulfide (VIII). The photolysis was shown to be due to the π-π^* excitation from the results of specific irradiation to π-π^* and n-π^* bands. The relative rates of photolysis of 2-nitrosoimino-3-phenyl-2,3-dihydrobenzothiazole (Ia) were measured in several solvents. The mechanism has been discussed in connection with that in alkyl nitrites and nitrosamines.

Simple *N*-nitrosoimines were not known until recently since they are unstable and decompose into the corresponding carbonyl compounds and nitrogen. In 1968, Thoman and Hunsberger prepared sterically hindered *N*-nitrosoketimines.[2] However, a few heterocyclic compounds carrying the nitrosoimino group stabilized by conjugation have been known to be stable at room temperature. They also decompose into the corresponding carbonyl compounds and nitrogen in refluxing toluene.[3]

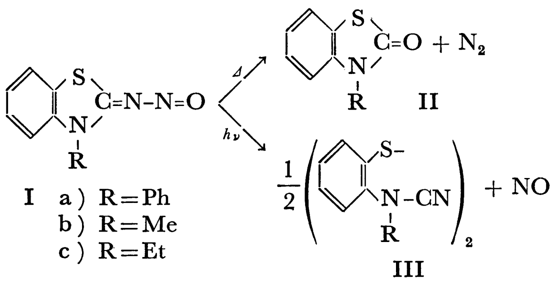
We wish to report that the photolysis of 2-nitrosoimino-2,3-dihydrothiazoles gives the corresponding disulfides through π-π^* excitation accompanied by the C-S bond cleavage and nitric oxide formation.

Results and Discussion

Reaction Products. 2-Nitrosoimino-3-phenyl-2,3-dihydrobenzothiazole (Ia) in benzene-dichloromethane was irradiated with a medium-pressure mercury lamp (100W) through a pyrex filter under nitrogen for 5 hr at about 10°C. Evolution of nitric oxide was observed during the irradiation. Bis[*o*-(*N*-phenylcyanamino)phenyl] disulfide (IIIa) was obtained in 74% yield.

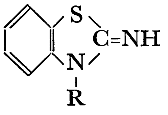
In the cases of 3-methyl- (Ib) and 3-ethyl-2-nitrosoimino-2,3-dihydrobenzothiazoles (Ic), the photolyses proceeded considerably more slowly than that of Ia. In order to suppress further decomposition of the resulting disulfides (IIIb and IIIc), irradiation was discontinued after 13—15 hr, during which time 50—60% of the starting nitrosoimines was consumed. The products were IIIb (48%) and IIIc (45%) together with 2-imino-2,3-dihydrobenzothiazoles (IVb, 17%, IVc, 5%). Irradiation of Ib for a longer period (20—25 hr) gave IVb (15%) and the corresponding immonium chloride (Vb, 37%), the formation of which showed formation of hydrogen chloride due to the decomposition of dichloromethane.

Photolysis of nitrosoimines (I) gave no 3-substituted 2,3-dihydro-2-benzothiazolones (II), showing that the photochemical reaction differs completely from that of a thermal one.

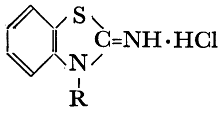


I　a) R=Ph
　b) R=Me
　c) R=Et

II　　III

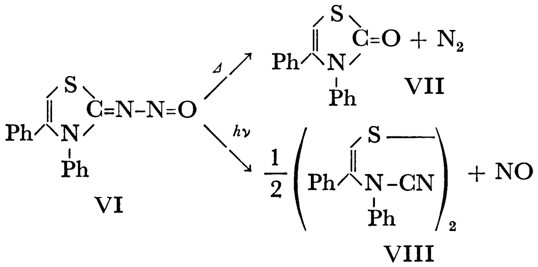


IV



V

3,4-Diphenyl-2-nitrosoimino-2,3-dihydrothiazole (VI) was also irradiated in acetonitrile for 30 min, 51% of VI being decomposed. Bis[(2-phenyl-2-*N*-phenylcyanamino)vinyl] disulfide (VIII) was obtained in 50% yield based on photolyzed VI. When it was irradiated for 50 min for completion, several compounds were detected by thin layer chromatography. Thiazolone (VII), the product in thermal decomposition of VI, was not produced at all during the photolysis.



VI　VII　VIII

Irradiation of nitrosoimine (Ia) in benzene-dichloromethane in the presence of cyclohexane (ten times of Ia in mol) gave the nitrate of 2-imino-3-phenyl-2,3-dihydrobenzothiazole in 20% yield, the structure of which was determined by elemental analysis and quantitative nitrosation to Ia with sodium nitrite and acetic acid. Formation of nitric acid may be due to the reaction of nitric oxide with hydrogen donor, cyclohexene, as shown in the following.

$$NO + C_6H_{10} \rightarrow HNO + C_6H_9\cdot$$

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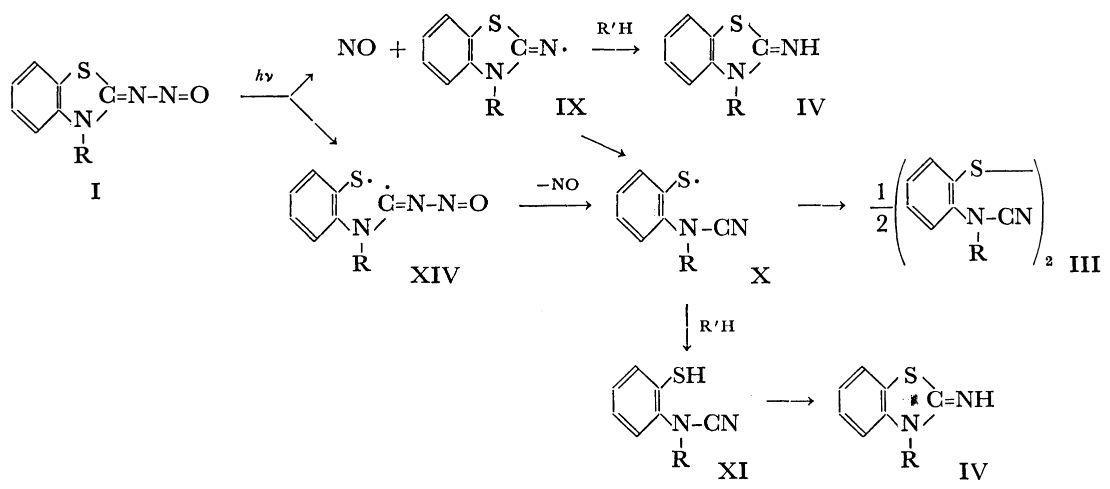
(1) For Part I: K. Akiba, I. Fukawa, K. Mashita, and N. Inamoto, *Tetrahedron Lett.*, **1968**, 2859.

(2) C. J. Thoman, S. J., and I. M. Hunsberger, *J. Org. Chem.*, **33**, 2852 (1968).

(3) a) H. Passing, *J. Parkt. Chem.*, **153**, I (1939). b) E. Besthorn, *Ber.*, **43**, 1523 (1910). c) W. Gebhart, *ibid.*, **17**, 2088 (1884). d) J. Goerdeler, A. Huppertz, and K. Wember, *Chem. Ber.*, **87**, 68 (1954).



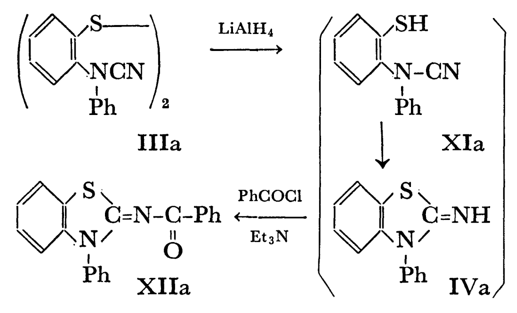
$$HNO + 2\,NO \rightarrow HNO_3 + N_2$$

The second reaction seems to be analogous to the formation of benzenediazonium nitrate from nitrosobenzene and nitric oxide.[4] Only black tar was obtained when oxygen was passed through the solution during the photolysis.

We propose a general scheme as given above.

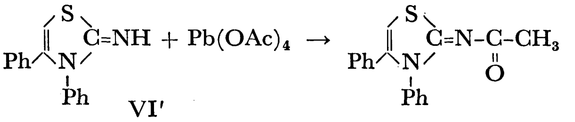
The presence of thiyl radical (X) is quite clear because of the formation of disulfide (III). Whether imino radical (IX) exists as a primary intermediate to give thiyl radical (X) or not cannot be determined in spite of isolation of imines (IV), because *o*-cyanaminothiophenol (XI) tends to cyclize to imine (IV) rapidly as shown below.

When IIIa was reduced with lithium aluminum hydride in tetrahydrofuran (THF) and benzoylated soon after with benzoyl chloride and triethylamine, 2-benzoylimino-3-phenyl-2,3-dihydrobenzothiazole (XII) was obtained in 68% yield. This shows that the intermediate thiophenol (XI) forms 2,3-dihydrothiazole ring (IVa) before it undergoes benzoylation.[5]

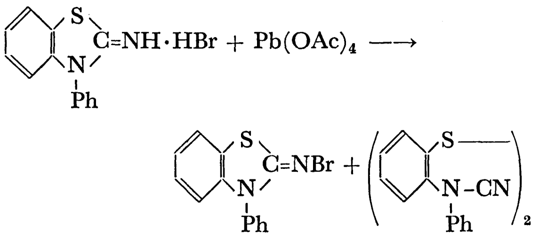


The results of oxidation of imines with lead tetraacetate are worth mentioning, although direct correlation between the oxidation and the proposed mechanism is not clear.

Oxidation of 3,4-diphenyl-2-imino-2,3-dihydrothiazole (VI′) with lead tetraacetate in benzene gave 2-acetylimino-3,4-diphenyl-2,3-dihydrothiazole in 35% yield with some unidentified products. In the case of the hydrochloride of imine VI′, the 2-acetylimino compound was obtained in 19% yield.



A similar oxidation of 2-imino-3-phenyl-2,3-dihydrobenzothiazole hydrobromide gave 2-*N*-bromoimino compound (XIII) and disulfide (IIIa) in 50% and 6.7% yields, respectively.



XIII IIIa

Kinetic Study. Ultraviolet and visible absorptions of 2-nitrosoimino-2,3-dihydrothiazoles (I and VI) are summarized in Table 1. Other absorptions of Ia in chloroform at 265 (ε 6.43×10^3), 273 (6.55×10^3) and 289 nm (4.21×10^3) are common to those of other compounds listed in Table 1 and attributed to excitation of the 2,3-dihydrothiazole ring.

TABLE 1. ULTRAVIOLET AND VISIBLE ABSORPTIONS OF 2-NITROSOIMINO-2,3-DIHYDROTHIAZOLES

Compound	Solvent	λ_{max} (nm)	ε	λ_{max} (nm)	ε
Ia	$CHCl_3$	354	1.18×10^4	506	62.2
Ib	$CHCl_3$	350	1.45×10^4	496	68.2
Ic	$CHCl_3$	350	1.28×10^4	496	65.0
VI	CH_3CN	350	1.08×10^4	454	111.0

Visible absorptions (450—520 nm) of the nitrosoimines shift toward the shorter wavelength (blue shift) by changing solvents from non-polar to polar ones (see Table 3), and are assigned to the n-π^* transition of the nitrosoimino group. The most intense absorptions at about 350 nm, which are not affected by

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[4] E. Bamberger, *Ber.*, **30**, 506 (1897).

[5] E. H. Rodd, "Chemistry of Carbon Compounds", Vol. IVa, Elsevier Publishing Co., Amsterdam (1957) p 425.

the polarity of the solvent (see Table 3), were assigned to the π-π^* transition of the nitrosoimino group, which is conjugated to the 2,3-dihydrothiazole ring. These assignments were supported by the fact that such absorptions were absent in the spectra of the corresponding 2-imino compounds. As an example, 2-imino-3-phenyl-2,3-dihydrobenzothiazole (IVa) showed the following absorption in chloroform: 281 (ε 5.3×10^3) and 288 nm (5.9×10^3).

2-Nitrosoimino-3-phenyl-2,3-dihydrobenzothiazole (Ia) was chosen as the substrate for most of the kinetic study, since its photolysis in various solvents produced disulfide (IIIa) in high yield (72—79%) and the π-π^* and n-π^* absorption bands were completely separate from one another.

Specific irradiation of the π-π^* and n-π^* bands of Ia was carried out in order to decide which excitation initiated the reaction (see Experimental). Irradiation of the π-π^* absorption region at 365 nm showed the same relative decomposition rates as those by a pyrex filter as shown in Table 2.

Table 2. Relative rates of photolysis of Ia with filters

Solvent	Filter		
	Pyrex	365 nm[a]	546 nm[b]
C_6H_6	2.3	2.3	—
CH_2Cl_2	1.0	1.0	—
CH_3CN	1.0	1.0	—

a) Aqueous solution of cobaltous sulfate and cupric sulfate.
b) Aqueous solution of calcium chloride and cupric chloride.

On the other hand, irradiation of the n-π^* absorption region at 546 nm for 5 hr did not initiate photoreaction at all, and led to complete recovery of the starting nitrosoimine (Ia), both in benzene and dichloromethane. Thus, the photoreaction of nitrosoimine (Ia) is completely due to the π-π^* excitation.

Quantum yield (0.38) was measured in acetonitrile by irradiation with 365 nm light.

The photolysis rates of I were then measured in various solvents with a pyrex filter. We chose the rate of Ia in acetonitrile (4.3×10^{-2} mmol/min) to be the standard value 1.0.

As shown in Fig. 1, plots of the nitrosoimine concentration against time showed a straight line. The linearity indicates that the amount of nitrosoimine (I) decomposed per unit time was constant. Because of intense π-π^* absorption, the solution of I absorbs 100% effective incident radiation at 365 nm.

As shown in Table 3, a greater decomposition rate of Ia was observed in aromatic solvents such as benzene, toluene and anisole, and the rates in non-aromatic solvents were almost constant in spite of the wide change of dielectric constants of the solvents. The decomposition rates of Ib and Ic were considerably less than that of Ia, and the rate of Ic was scarcely accelerated at all in benzene.

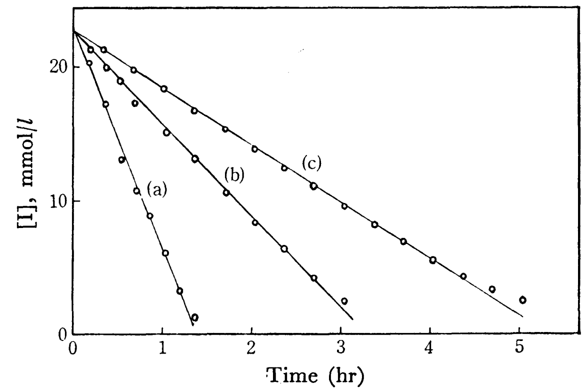


Fig. 1. Photolysis of the nitrosoimines (I).
(a) Ia in C_6H_6; (b) Ia in CH_3CN; (c) Ic in CH_3CN

Aromatic solvents might not act as a photosensitizer for Ia, because the rate in a mixture of benzene and acetonitrile is equal to that in acetonitrile. Benzene is completely transparent and not photochemically

Table 3. Relative photolysis rates and electronic spectra of 3-substituted 2-nitrosoimino-2,3-dihydrobenzothiazole(I) in various solvents (λ_{max} by nm)

I (7.8 mmol)	Solvent (350 ml)	Relative rate	n-π^* λ	n-π^* ε	π-π^* λ	π-π^* ε
Ia	C_6H_6	2.3	521	57.8	353	1.40×10^4
Ia	$C_6H_5CH_3$	2.3	522	53.9	353	1.26×10^4
Ia	$C_6H_5OCH_3$	1.4	519	60.0	354	1.32×10^4
Ia	C_6H_6-CH_3CN (2 : 5)[a]	1.0	508	57.9	351	1.41×10^4
Ia	CH_3CN	1.0[b]	508	57.9	351	1.41×10^4
Ia	CH_2Cl_2	1.0	508	61.3	353	1.27×10^4
Ia	$CHCl_3$	1.1	506	62.5	354	1.18×10^4
Ia	C_2H_5OH-CH_2Cl_2 (5 : 2)[a]	1.2	491	63.4	351	1.20×10^4
Ia	CH_3OH-CH_2Cl_2 (5 : 2)[a]	1.2	484	64.9	351	1.39×10^4
Ib	C_6H_6	0.5	513	56.9	349	1.59×10^4
Ic	C_6H_6	0.7	512	58.3	349	1.55×10^4
Ic	CH_3CN	0.6	501	60.4	349	1.36×10^4

a) Volume ratio of the solvents.
b) Rate, 4.3×10^{-2} mmol/min, was taken to be the standard rate 1.0.

Table 4. Absorption spectra of unsaturated compounds of nitrogen

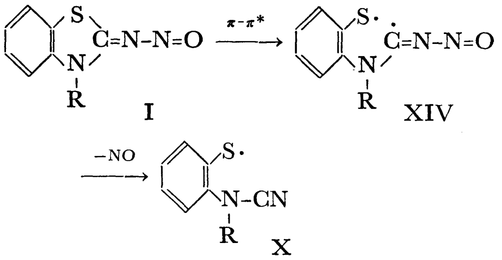
Compound	Solvent	*n*-π*	π-π*	Ref.
Ib	$CHCl_3$	496 (68.2)	350 (14500)	a
VI	CH_3CN	454 (111)	350 (10800)	a
$(Ph_2N)_2C=N-N=O$	$CHCl_3$	519 (183)	330 (9550)	b
$(p\text{-}ClC_6H_4)_2C=N-N=O$	CCl_4	596 (107), 522 (107)	306 (8770)	2
$p\text{-}MeC_6H_4$, $o\text{-}MeC_6H_4$ $>C=N-N=O$	EtOH	520 (33), 494 (24)	312 (8414)	2
Ph-N=N-Ph(*trans*)	EtOH	443 (510)	320 (21300)	7
$Ph_2C=NH$	$CHCl_3$	340 (125)		7
t-Bu-N=O	EtOEt	665 (20), 300 (100)		7
$Me_2N-N=O$	C_5H_{12}	361 (125)	232 (5900)	7
t-Bu-O-N=O	C_5H_{12}	356 (87)	222 (1700)	7
$Ph-NO_2$	C_6H_{14}	330 (125)	280 (1000)	7

a) The present work. b) Unpublished result.

excited at all by irradiation with 365 nm.

Since an interaction of *N*-nitrosamines with the solvent benzene was observed by NMR,[6] the solvent effect on the decomposition rate of Ia might also be ascribed to an interaction of nitrosoimine with the aromatic solvents. However, this explanation is not consistent with the fact that the rate of Ic is scarcely accelerated at all in benzene. The reason for the specific acceleration of photolysis rate of Ia in aromatic solvents is not yet clear.

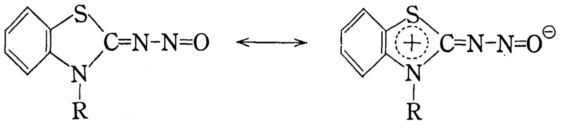
From the results, we propose that the photolysis of the nitrosoimines is due to π-π* excitation, and some radical intermediate (X) is produced according to the ring opening followed by loss of nitric oxide from the resulting biradical (XIV).



General Discussion. Compounds containing the double-bonded nitrogen group, such as nitroso, azo, and imino compounds, have weak absorptions in the longer wavelengths due to the *n*-π* excitation of the non-bonding nitrogen electrons, as shown in Table 4.

Thoman and Hunsberger reported that the absorption spectra of di(*p*-chlorophenyl)-nitrosoiminomethane showed two visible absorptions at 596 and 522 nm, probably due to the *n*-π* excitations of nitrogens of the nitroso and imino parts of the nitrosoimino group, respectively.[2] On the other hand, heterocyclic nitrosoimino compounds show apparently only one *n*-π* absorption at a shorter wavelength than di(*p*-chlorophenyl)-nitrosoiminomethane.

In the case of the heterocyclic nitrosoimino compounds such as I, the two lone pairs of N-atoms might be nearly equivalent with respect to their electronic energy and the two *n*-π* bands might overlap each other. As a result, only one apparent *n*-π* excitation was observed as with the azo compound, indicating that the resonance structure (I′) appears to be predominant.



A large contribution of I′ is supported by the fact that 2,3-dihydrothiazoles are one of the "π-electron excess aromatic compounds". The thermal stability of I is consistent with resonance stabilization. The nitrosoimino group of I shows the π-π* absorption at a longer wavelength (*ca.* 350 nm) than that of di(*p*-chlorophenyl)-nitrosoiminomethane (*ca.* 306 nm), indicating a high degree of conjugation with the 2,3-dihydrothiazole ring. The fact that absorption bands of di(diphenylamino)-nitrosoiminomethane lie between those of the above two cases shows resonance contribution of nitrogens in the diphenylamino group.

Thus, the photoreaction of I is due to π-π* excitation, but does not occur by the irradiation of *n*-π* absorption. This result is in significant contrast to photoreactions of nitrites[8] or nitrosoalkanes[9] which lead to the cleavage of RO-NO bond or C-NO bond with high quantum yield even by the irradiation of their *n*-π* bands to give alkoxyl or alkyl radical together with nitric oxide, respectively.

The different behavior of nitrosoimine is ascribable to the fact that its N-N bond has a strong double bond character with a larger bond energy than O-N and C-N bond of the nitrites and the nitrosoalkanes, respectively.

N-Nitrosamines are inert for photolysis in neutral

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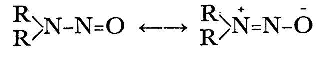
[6] C. J. Karabatos and R. A. Taller, *J. Amer. Chem. Soc.*, **86**, 4373 (1964).

[7] S. F. Mason, *Quart. Rev.*, **15**, 314 (1961).

[8] M. Akhtor and D. H. R. Barton, *J. Amer. Chem. Soc.*, **86**, 1528 (1964); M. Akhtor, "Advances in Photochemistry", **2**, 263 (1964).

[9] K. D. Anderson, C. J. Crumpler, and D. L. Hammick, *J. Chem. Soc.*, **1935**, 1679.

and in strong acidic media.[10] This is explained by a similar double bond character of the N-N bond both in the photoexcited state and in strong acidic media as shown below.



$$\mathrm{R_2N{-}N{=}O \longleftrightarrow R_2\overset{+}{N}{=}N{-}\overset{-}{O}}$$

These considerations support the idea that the π-π^* irradiation of nitrosoimine induces a cleavage of the C-S bond of the 2,3-dihydrothiazole ring followed by that of N-N bond of the nitrosoimino group to give directly thiyl radical (X) and nitric oxide. However, there is no definite evidence at present to exclude the mechanism involving the photochemical cleavage of the N-N bond of the nitrosoimino group to give nitric oxide and the vibrationally excited imino radical (IX), which isomerizes into more stable thiyl radical (X).

Experimental

Materials. 2-Imino-3-phenyl-2,3-dihydrobenzothiazole (IVa) was prepared by the method of Passing,[3a] mp 73—74°C (lit, 74—75°C). 2-Nitrosoimino-3-phenyl-2,3-dihydrobenzothiazole (Ia) was prepared by nitrosation of IVa in acetic acid with a concentrated aqueous solution of sodium nitrite, and then reprecipitated twice from dichloromethane solution by adding petroleum ether, mp 138°C (decomp.) (lit,[3a] mp 141°C). 2-Imino-3-methyl- (IVb) and 3-ethyl-2-imino-2,3-dihydrobenzothiazole (IVc), 3-methyl-2-nitrosoimino- (Ib) and 3-ethyl-2-nitrosoimino-2,3-dihydrobenzothiazole (Ic) were prepared according to reported procedures.[3b,3c] IVb: mp 122—123°C (lit, 123°C), IVc: mp 86—87°C (lit, 86°C), Ib: 104—105°C (decomp.) (lit, 103—104°C), and Ic: mp 108—109°C (decomp.) (lit, 110°C).

3,4-Diphenyl-2-imino-2,3-dihydrothiazole hydrochloride and the corresponding free imine (mp 107°C, lit, 111°C) were prepared according to the method of Beyer and Ruling.[11] 3,4-Diphenyl-2-nitrosoimino-2,3-dihydrothiazole (VI) was prepared by nitrosation of hydrochloride in 42% yield, mp 152—153°C (decomp.).

Found: C, 63.74; H, 4.20; N, 14.67%. Calcd for $C_{15}H_{11}N_3SO$: C, 64.04; H, 3.93; N, 14.94%.

General Procedure of Photolysis. The nitrosoimines were irradiated through a pyrex filter with a 100W medium-pressure mercury lamp immersed in the reaction solution. The temperature of the solution was kept at *ca.* 10°C with a water-cooled jacket around a lamp and an external ice bath. Nitrogen was passed through the solution during irradiation.

Photolysis of 2-Nitrosoimino-3-phenyl-2,3-dihydrobenzothiazole (Ia). a) Nitrosoimine (Ia, 4.0 g, 15.7 mmol) in a mixture of benzene (50 m*l*)-dichloromethane (100 m*l*) was irradiated. Irradiation was stopped when the absorption at 350—360 nm region disappeared completely. The crystalline product obtained after evaporation of the solvent was recrystallized from ethanol to give bis[*o*-(*N*-phenylcyanamino)phenyl] disulfide (IIIa, 2.2 g, 5.8 mmol, 74%); mp 151.5—152.0°C and IR: 2200 cm^{-1} (C≡N).

Found: C, 69.15; H, 4.16; N, 12.64; S, 14.23%. mol wt (Rast), 410. Calcd for $C_{26}H_{18}N_4S_2$: C, 69.31; H, 4.03; N, 12.44; S, 14.23%; mol wt, 450.

b) Nitrosoimine (Ia, 4.0 g, 15.7 mmol) in a mixture of benzene (50 m*l*)-dichloromethane (100 m*l*) was irradiated in the presence of cyclohexene (157 mmol). Removal of volatile materials gave the immonium nitrate of 2-imino-3-phenyl-2,3-dihydrobenzothiazole (3.1 mmol, 20%), mp 198°C (decomp.), after washing with benzene.

Found: C, 53.77; H, 3.54; N, 14.89%. Calcd for $C_{13}H_{11}N_3SO_3$: C, 53.97; H, 3.83; N, 14.51%.

Nitrosation of the immonium nitrate with sodium nitrite and acetic acid gave Ia quantitatively. The benzene washings were evaporated and the brown residual oil was chromatographed on alumina. No crystalline product was obtained. The infrared spectrum of the oil showed a strong absorption at 2200 cm^{-1} (C≡N) indicating the presence of IIIa.

Reduction of Disulfide (IIIa) with $LiAlH_4$. A solution of lithium aluminum hydride (0.5 g, 33.3 mmol) in THF (50 m*l*) was added in small portions to the disulfide (IIIa, 1.5 g, 3.3 mmol) in THF (50 m*l*) cooled with an ice bath. After the addition had been completed, the reaction mixture was stirred for 1 hr. The remaining lithium aluminum hydride was decomposed by adding aqueous solution of sodium hydroxide (20%, 1 m*l*) and then water (15 m*l*). After filtration, the precipitates were extracted with dichloromethane (150 m*l*) and the combined solution was dried over anhydrous sodium sulfate. The concentrated solution (50 m*l*) was refluxed with triethylamine (1.5 g, 16.4 mmol) and benzoyl chloride (1.5 g, 10.7 mmol) for 1 hr, and 100 m*l* of dichloromethane was then added. After shaking several times with 1 N aqueous solution of sodium hydroxide (40 m*l*) to remove excess benzoyl chloride, the dichloromethane layer was washed with water and dried over anhydrous sodium sulfate. The pale yellow solid obtained after evaporation of the solvent was recrystallized from ethanol to give 2-benzoylimino-3-phenyl-2,3-dihydrobenzothiazole (XIIa, 1.5 g, 4.5 mmol, 68%), mp 205.5—206.5°C. IR: 1620 cm^{-1} (C=O).

Found: C, 72.72; H, 3.99; N, 8.50%. Calcd for $C_{20}H_{14}N_2SO$: C, 72.70; H, 4.28; N, 8.48%. XIIa was identified by comparison with the melting point and IR spectrum of an authentic sample, prepared by a similar benzoylation of 2-imino-3-phenyl-2,3-dihydrobenzothiazole (IVa).

Photolysis of 3-Methyl-2-nitrosoimino-2,3-dihydrobenzothiazole (Ib). Nitrosoimine (Ib, 6.0 g, 30.9 mmol) in a mixture of benzene (50 m*l*) and dichloromethane (100 m*l*) was irradiated for 17 hr, during which time 60% of Ib was consumed. After evaporation of the solvent, the residue was extracted with petroleum ether (200 m*l*). The extract was concentrated *in vacuo* at room temperature and the resulting precipitates were recrystallized from petroleum ether to give 2-imino-3-methyl-2,3-dihydrobezothiazole (IVb, 0.6 g, 3.1 mmol, 17%), mp 122—123°C. The remaining crystalline residue was refluxed in ethanol for 8 hr to decompose the remaining nitrosoimine (Ib) into 3-methyl-2,3-dihydro-2-benzothiazolone (IIb). After evaporation of the solvent, the residue was extracted repeatedly with petroleum ether to remove IIb. The remaining white solid was recrystallized from ethanol to give bis[*o*-(*N*-methylcyanamino)-phenyl] disulfide (IIIb, 1.4 g, 4.3 mmol, 48%), mp 140.0—141.0°C. IR: 2200 cm^{-1} (C≡N).

Found: C, 58.90; H, 4.34; N, 17.27; S, 19.52%; mol wt (Rast), 376. Calcd for $C_{16}H_{14}N_4S_2$: C, 58.87; H, 4.32; N, 17.17; S, 19.64%; mol wt, 326.

Photolysis of 3-Ethyl-2-nitrosoimino-2,3-dihydrobenzothiazole (Ic). Ic (6.0 g, 29.2 mmol) was irradiated in a mixture of benzene (50 m*l*) and dichloromethane (100 m*l*) for 13 hr, 60% of Ic being consumed. A treatment similar to that

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[10] E. M. Burgess and J. M. Lavanish, *Tetrahedron Lett.*, **1964**, 1221; Y. L. Chow, *idid.*, **1964**, 2333; **1965**, 2473; *Can. J. Chem.*, **43**, 2711 (1965); L. P. Kuhn, G. G. Kleinspehn, and A. C. Duckworth, *J. Amer. Chem. Soc.*, **89**, 3858 (1967).

[11] H. Beyer and G. Ruling, *Chem. Ber.*, **89**, 107 (1956).

for Ib gave 3-ethyl-2-imino-2,3-dihydrobenzothiazole (IVc, 0.2 g, 0.9 mmol, 5%), mp 86—87°C, and bis[*o*-(*N*-ethylcyanamino)phenyl] disulfide (IIIc, 1.4 g, 4.0 mmol, 45%), mp 83.0—84.0°C, and IR: 2200 cm^{-1} (C≡N).

Found: C, 60.97; H, 5.17; N, 15.67; S, 17.83%; mol wt (Rast), 364. Calcd for $C_{18}H_{18}N_4S_2$: C, 60.81; H, 5.39; N, 15.76; S, 18.04%; mol wt 354.

Photolysis of 3,4-Diphenyl-2-nitrosoimino-2,3-dihydrothiazole (VI). A solution of nitrosoimine (VI, 1.165 g, 4.15 mmol) in acetonitrile (250 m*l*) was irradiated for 30 min, 51% of the starting material being photolyzed. Photolysis on the same scale was repeated four times. Solutions from two runs were combined and treated as follows.

The solvent (500 m*l*) was evaporated with a rotary evaporator to 50 m*l*. The resulting yellow precipitates (0.728 g, VI) were filtered and the filtrate was condensed to almost dryness. A mixture of petroleum ether (110 m*l*) and ethanol (10 m*l*) was added to the residue and the resulting precipitates (0.484 g, VI) were filtered. White crystalline product (0.643 g, almost pure VIII) and brown tar (0.6 g) were obtained from the filtrate by condesation. In order to purify the crystalline product, the main fractions of R_f 0.6—0.7 (with chloroform) were collected on silica gel thin layer chromatograms and extracted with methanol (30 m*l*). The extract was condensed to 10 m*l* to give bis[(2-phenyl-2-phenylcyanamino)vinyl] disulfide (VIII, 0.510 g), mp 141.0—142.0°C. IR: 2210 cm^{-1} (C≡N), UV: $\lambda_{max}^{CHCl_3}$ 280 nm (ε 3.47×10^4) and MS: 476 (5.5%, M$^+$−CN), 251 (62, 1/2 M$^+$), 180 (99, $PhC{\equiv}\overset{+}{N}Ph$), 134 (26, PhCHCS$^+$), 91 (10.5, PhN$^+$), 77 (100, Ph$^+$), and 26 (50, CN$^+$).

The parent peak (M$^+$, 502) could not be detected in spite of some change in the ionization voltage. The yield of VIII was 50% based on the photolyzed material.

Thermal Decomposition of 3,4-Diphenyl-2-nitrosoimino-2,3-dihydrothiazole (VI). Nitrosoimine (VI, 1.02 g, 3.63 mmol) was refluxed in xylene (50 m*l*) until the orange-red color of VI disappeared. Removal of the solvent gave 0.67 g (2.65 mmol, 73%) of the corresponding thiazolone (VII) as colorless crystals, mp 121.5—123°C. IR (nujol): 1640 cm^{-1} (C=O). Found: C, 71.00; H, 4.35; N, 5.28; S, 12.70%. Calcd for $C_{15}H_{11}NOS$: C, 71.12; H, 4.38; N, 5.53; S, 12.66%.

Oxidation of 3,4-Diphenyl-2-imino-2,3-dihydrothiazole (VI′) with Lead Tetraacetate. To a benzene solution (40 m*l*) of the imine (VI′, 4.0 g, 16.0 mmol), lead tetraacetate (5.5 g, 12.4 mmol) was added portionwise at 0°C with stirring which was continued overnight at room temperature. After filtration of yellow crystals (lead acetate, 3.5 g), the filtrate was condensed with a rotary evaporator. The condensate was chromatographed on silica gel to give 2-acetylimino-3,4-diphenyl-2,3-dihydrothiazole (1.66 g, 4.34 mmol), mp 200°C, in 35% yield, which was eluted with dichloromethane-ether (4 : 1). An authentic sample of 2-acetylimino compound (mp 200°C) was prepared according to the method of Beyer and Ruling.[11] There were some unidentified products.

The hydrochloride of imine (VI′) was oxidized with lead tetraacetate in a similar way to that above. The 2-acetylimino compound was obtained in 19.0% yield with some unidentified products.

Oxidation of 2-Imino-3-phenyl-2,3-dihydrobenzothiazole Hydrobromide with Lead Tetraacetate. To a suspension of the imine hydrobromide (4.0 g, 13.0 mmol) in benzene (30 m*l*), lead tetraacetate (4.0 g, 18.2 mmol) was added portionwise at room temperature with stirring, which was continued overnight. Lead tetraacetate was consumed completely as confirmed by iodometry. After the yellow precipitates, lead acetate (3.64 g), were filtered, the filtrate was condensed and the condensate was chromatographed on silica gel. *N*-Bromoimino-3-phenyl-2,3-dihydrobenzothiazole (XIII, 2.0 g, 6.5 mmol, 50% yield) was eluted with benzene and the disulfide (IIIc, 0.20 g, 2.1 mmol, 6.7%) was eluted with benzene-dichloromethane. XIII: mp 139°C (decomp.), UV: $\lambda_{max}^{CH_3CN}$ 263 nm (ε 1.48×10^4) and MS: 306 (M$^+$), 304 (M$^+$) and 225 (M$^+$−Br, 100).

Found: C, 51.10; H, 2.78; N, 9.41; S, 10.13%. Calcd for $C_{13}H_9N_2SBr$: C, 51.16; H, 2.77; N, 9.18; S, 10.50%.

Kinetic Studies. The photolysis rates of the nitrosoimines (I, 7.8 mmol) were measured in several solvents (350 m*l*) with the same apparatus. The concentration of the remaining nitrosoimines (I) was measured by UV absorption at *ca.* 350 nm at appropriate intervals. Because of the poor solubility of I in alcohols, the mixed solvents of ethanol (250 m*l*)-dichloromethane (100 m*l*) were used. The electronic spectra of nitrosoimine (Ia) in alcohols were not affected by the addition of dichloromethane. 3.9 mmol of Ia was used in the case of toluene (350 m*l*).

The decomposition rate of Ia in acetonitrile (4.31×10^{-2} mmol/min) was chosen to be the standard relative rate 1.0. Two filter solutions were used for the specific irradiation of π-π^* and n-π^* absorption bands. They were cooled with an ice bath and circulated through a cooling jacket (path length 1 cm) around the lamp, instead of with water. An aqueous solution of cobaltous sulfate and cupric sulfate (a mixture of 490 g of $CoSO_4 \cdot 7H_2O$, 100 g of $CuSO_4 \cdot 5H_2O$ and 900 m*l* of H_2O)[12] was used as one filter solution for isolation of 365 nm radiation from a medium-pressure mercury lamp.

The decomposition rates of Ia in benzene solution with unfiltered light and filtered light (π-π^* irradiation) were 9.3×10^{-2} and 8.5×10^{-2} mmol/min, respectively. The reduced rate of the latter corresponds to the transmittance of the filter solution (Fig. 2).

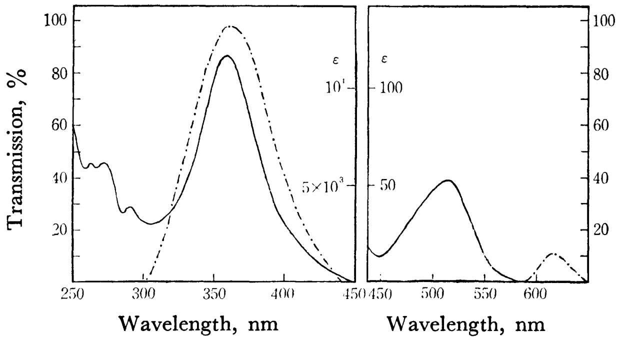

Fig. 2. Electronic spectrum of Ia in $CHCl_3$ (solid line) and transmission of the filter solution (dotted line; $CoSO_4$-$CuSO_4$)

An aqueous solution of cupric chloride and calcium chloride (100 g of $CuCl_2$, 300 g of $CaCl_2$ in 1 *l* of aqueous solution, slightly acidified with HCl) was used as the other filter solution for the isolation of the n-π^* absorption band at 546 nm. This filter solution transmitted 60% at 546 nm and 25% at 577 nm and no light was transmitted at either a wavelength shorter than 500 nm or one longer than 600 nm. No photodecomposition of Ia was observed with the use of this filter solution both in benzene and in dichloromethane. The transmission of both filters remained unchanged with time.

Quantum Yield Measurement. The isolation of 365 nm radiation from a medium-pressure mercury lamp (100 W) was accomplished by a combination of the filter solution

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[12] J. G. Calvert and J. N. Pitts, "Photochemistry," Chapter 7, John Wiley & Sons, Inc., New York (1967).

(120 g of $Cu(NO_3)_2$ in 100 ml of H_2O, path length 1 cm) and a Corning glass filter(No. CS-7-607). The transmission was 0% below 355 nm, 57% at 365 nm, and 0% above 400 nm. The light intensity was measured by potassium ferrioxalate actinometry¹³⁾ and was 2×10^7 Einstein l^{-1} sec^{-1}. The quantum yields of photolysis of Ia in acetonitrile were 0.384 and 0.372 by repeated determinations.

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13) C. A. Parker, *Proc. Roy. Soc., Ser. A*, **220**, 104 (1953); C. G. Hatchard and C. A. Parker, *ibid., Ser. A*, **235**, 518 (1956).