Tetrahedron Letters No.24, pp. 2859-2862, 1968. Pergamon Press. Printed in Great Britain.

FORMATION OF BIS[o-(N-SUBSTITUTED CYANAMINO)PHENYL] DISULFIDES BY PHOTOLYSIS OF 3-SUBSTITUTED 2-NITROSOIMINO-2,3-DIHYDROBENZOTHIAZOLES

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(Received in Japan 22 February 1968; received in UK for publication 18 March 1968)

3-Substituted 2-nitrosoimino-2,3-dihydrobenzothiazoles (I) have been known to decompose thermally into the corresponding 2,3-dihydrobenzothiazolones (II) and nitrogen (1). Now we wish to report the photochemical reaction of I, which proceeds through the initial cleavage of nitric oxide and produces diphenyl disulfide derivatives.

UV spectra of the nitrosoimines (I) are shown in Table I.

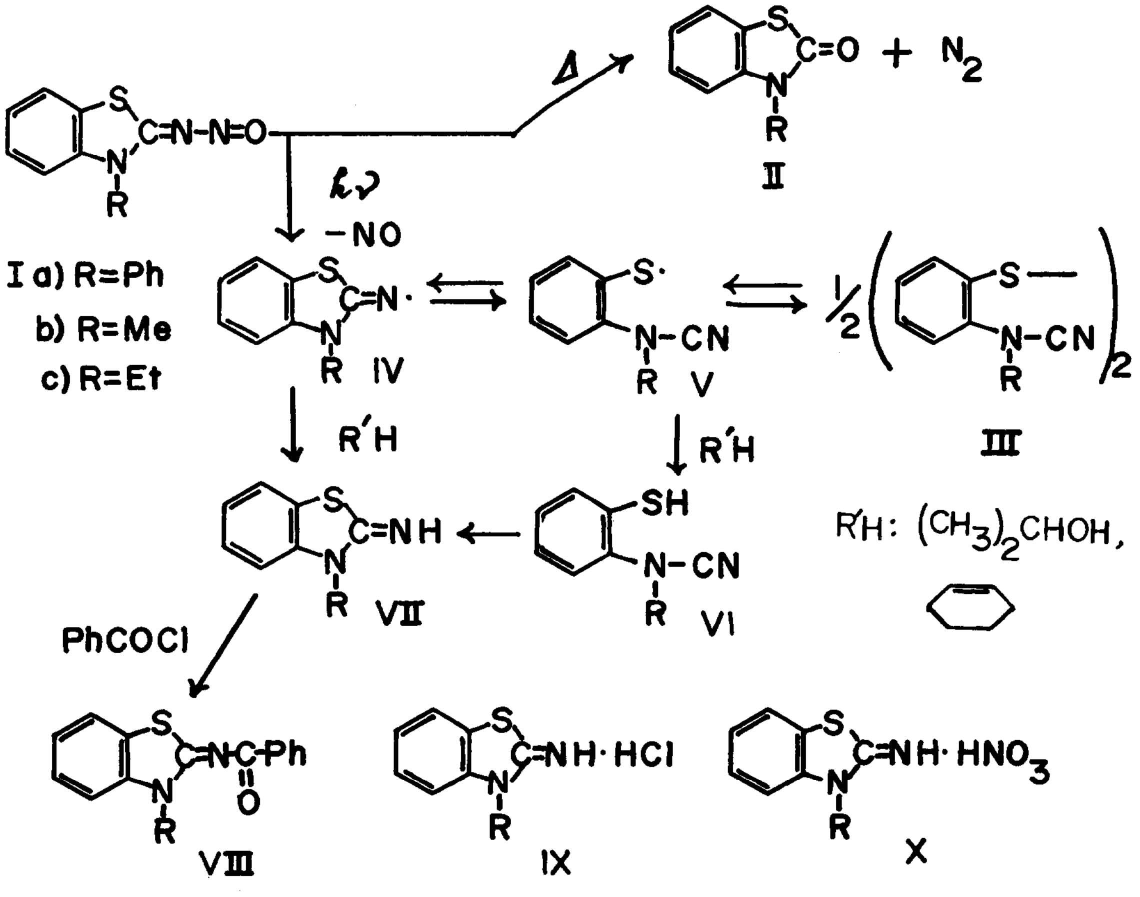
Table I UV spectra of 3-substituted 2-nitrosoimino-2,3-dihydrobenzothiazoles (I) (in $CHCl_3$; λ by mμ)

I	λ	ε	λ	ε	λ	ε	λ	ε	λ	ε
a) R=Ph	265	6.43×10^3	273	6.55×10^3	289	4.21×10^3	354	1.18×10^4	498	62.2
b) R=Me	265	7.14×10^3	272	7.70×10^3	289	4.27×10^3	350	1.45×10^4	496	68.4
c) R=Et	265	6.00×10^3	272	6.45×10^3	289	3.56×10^3	350	1.28×10^4	496	65.0

2-Nitrosoimino-3-phenyl-2,3-dihydrobenzothiazole (Ia, 15.7 mmol) was irradiated for 5 hours with high-pressure mercury lamp (100 W) in benzene (50 ml)-dichloromethane (100 ml) under nitrogen atmosphere at about 10°C. After evaporation of the solvent, the residue was extracted with petroleum ether (50 ml) and recrystallized from ethanol to yield bis[o-(N-phenylcyanamino)phenyl] disulfide (IIIa, 5.8 mmol, 74%). In the petroleum extract, no 2,3-dihydrobenzothiazolone (IIa) was obtained, showing that photochemical reaction differs completely from that of thermal one.

In the case of 3-methyl- (Ib) and 3-ethyl-nitrosoimine (Ic), these reactions were considerably slower than Ia. Therefore, in order to avoid further decomposition of the resulting disulfides (IIIb and IIIc), the irradiation was stopped after 13~15 hours, when 50~60% of the starting nitrosoimines had been consumed. By similar treatment to that of Ia, IIIb (48%) and IIIc (45%) were obtained. But in those cases, 2-imino-2,3-dihydrobenzothiazoles (VIIb, 17%; VIIc, 5%) were obtained from petroleum extracts, which were presumably due to the decomposition of IIIb and IIIc. When Ib was irradiated for more longer time (20~25 hours), VIIb (15%) and the corresponding immonium chloride (IX, 37%) were obtained. The acid is considered to be generated from the decomposition of dichloromethane.

These reactions can be rationalized by the following scheme and the properties of the disulfides (III) are shown in Table II.



In order to trap the intermediate radicals (IV or V), Ia was irradiated in the presence of hydrogen donors. When Ia (15.7 mmol) was irradiated in the presence of isopropyl alcohol (94.2 mmol) and benzoyl chloride (94.2 mmol) under the same condition as mentioned above, 2-benzoylimino-3-phenyl-2,3-dihydrobenzothiazole (VIIIa, 11.2 mmol, mp 205.5~6.0°C) was obtained in 71% yield. No depression of the melting point was observed when mixed with an authentic sample, which was prepared from VIIa and benzoyl chloride. And when Ia (15.7 mmol) was irradiated in the presence of cyclohexene (157 mmol), the corresponding immonium nitrate (X, 3.1mmol, decompose at 198°C) was obtained, and by nitrosation of X with sodium nitrite and acetic acid, Ia was obtained quantitatively. The formation of nitric acid may be ascribed to the following reaction, which is analogous to the formation of benzenediazonium nitrate from nitrosobenzene and nitric oxide (2). $HNO + 2\ NO \longrightarrow HNO_3 + N_2$

Table II Identification of the Disulfides (III)

III	mp	IR		Elemental Analyses (%)				MW*
	°C	ν_{CN} cm^{-1}		C	H	N	S	
a) R=Ph	151.5	2200	calcd	69.31	4.03	12.44	14.23	450
	~152.0		found	69.15	4.16	12.64	14.23	410
b) R=Me	140.0	2200	calcd	58.87	4.32	17.17	19.64	326
	~141.0		found	58.90	4.34	17.27	19.52	376
c) R=Et	83.0	2200	calcd	60.81	5.39	15.76	18.04	354
	~84.0		found	60.97	5.17	15.67	17.83	364

* Determined by Rast method

From these facts, it is apparent that 2-imino-2,3-dihydrobenzothiazole (VIIa) is formed in high yield in the presence of an appropriate hydrogen donor, but whether VIIa results from imino-radical (IVa) or thiyl-radical (Va) is not clear, because thiophenol (VIa) seems to change into 2-imino-2,3-dihydrobenzothiazole (VIIa) rapidly (3).

This is also supported by the fact that when Ia was reduced with $LiAlH_4$ in THF solution and benzoylated soon after with benzoyl chloride and triethylamine, VIIIa was obtained in 68% yield. This fact implies that the intermediate thiophenol (VIa) forms thiazole ring (VIIa) before it suffers benzoylation.

The yield of III reduced considerably when the substitution of the atmosphere for nitrogen was not sufficient, and under the stream of oxygen the yield reduced to zero and only brown tar was obtained. Benzene and benzophenone do not affect the reaction and further study on these mechanistic points is now in progress.

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