Chemistry of Nitrosoimines. XIV.[1] Photolysis of 5-Nitrosoimino-4-phenyl-3-phenylimino-1,2,4-thiadiazolidine

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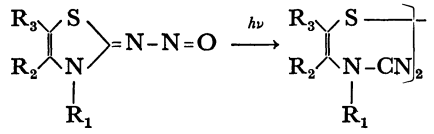
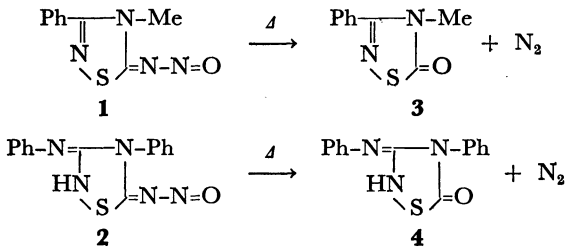
Photolysis of 5-nitrosoimino-4-phenyl-3-phenylimino-1,2,4-thiadiazolidine proceeded through π-π^* excitation and gave phenylcyanamide and 5-imino-4-phenyl-3-phenylimino-1,2,4-thiadiazolidine as primary products. It was found that other products were produced by the reactions of the primary products. The formation mechanisms have been discussed briefly.

In a previous paper,[2] we reported that photolysis of 2-nitrosoimino-2,3-dihydro-1,3-thiazoles gave the corresponding disulfides *via* π-π^* excitation.



As the extention of these works, this paper describes photolysis of 4-methyl-5-nitrosoimino-3-phenyl-1,2,4-thiadiazoline (**1**) and 5-nitrosoimino-4-phenyl-3-phenylimino-1,2,4-thiadiazolidine (**2**).

Similarly to other nitrosoimines,[3] the nitrosoimines **1** and **2** decomposed thermally to give 4-methyl-3-phenyl-1,2,4-thiadiazolin-5-one (**3**) and 4-phenyl-3-phenylimino-1,2,4-thiadiazolidin-5-one (**4**), respectively, in almost quantitative yields.



Photolysis of **1** was very slow in benzene or dichloromethane–acetone under an irradiation with a 100 W medium-pressure mercury lamp and gave a lot of products in small quantities, some of them containing cyano group (determined by IR). Therefore, the further investigation was given up, but this fact presumably supports that the photolyses of the nitrosoimino substituted heterocycles proceed through the π-π^* excitation, because the π-π^* absorption (317.5 nm) of **1** does not overlap effectively with 334.1 nm of the mercury arc.

The photolysis of **2** was carried out under several conditions. The results are summarized in Table 1.

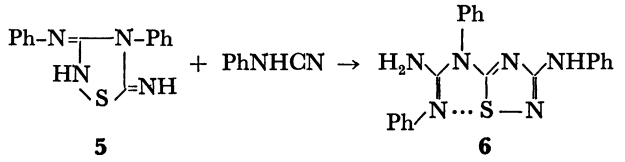
The reaction products were **5**—**11** and phenylcyanamide, depending on the reaction conditions. The compound **5** was identical with 5-imino-4-phenyl-3-phenylimino-1,2,4-thiadiazolidine, the denitrosation product of **2**. The compound **6** was the same as the 1 : 1 adduct of **5** and phenylcyanamide.[4] The compound **7** was determined to be 3,5-dianilino-1,2,4-thiadiazole by comparison with an authentic sample.[5] The compound **8** was identical with the reaction product of **5** with cyanic acid, 5-carbamoylimino-4-phenyl-3-phenylimino-1,2,4-thiadiazolidine. The compounds **9** and **10** were determined to be phenylurea and phenylisomelamine, respectively. The structure of **11** remains

Table 1. Photolyses of **2**

Run	1[a]	2	3	4[b]
Reaction condition				
2 (mmol)	6.1	34.4	20.4	29.8
Solv. (ml)	CH_2Cl_2 (900)	PhH-DMF (2 : 1) (1400)	PhH-*i*-PrOH-DMF (5 : 5 : 7) (850)	*i*-PrOH-DMF (1 : 1) (1100)
Lamp (W)	100	100	100	400
Filter	Pyrex	Pyrex	filter soln.[c]	filter soln.[c]
Reac. Time (hr)	6	40	20	3
Reac. Temp. (°C)	20—25	5—10	5—10	10—15
Product, mmol (%)				
5	0.3(5)			
6	0.7(17.2)	4.4(19.2)	1.1 (8.1)	2.0(10.1)
7		3.7(10.8)	0.45(2.2)	
8		1.9(11.0)		
9		6.0(8.8)	2.8 (6.8)	4.3(7.2)
10			0.28(2.1)	
11		1.1(3.3)	2.8(13.7)	+
PhNHCN				12.0(20.2)

a) Other products were not identified. b) About 5 mmol of **2** was recovered (16.8%). c) For 340—360 nm. See Ref. 2.

unknown.



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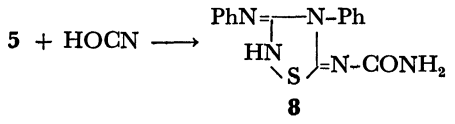

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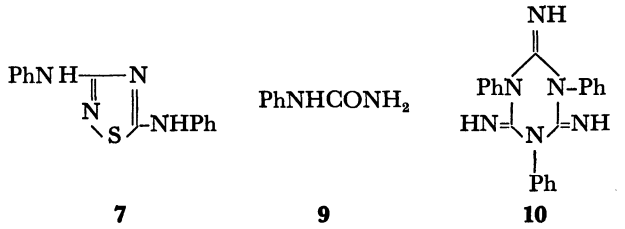
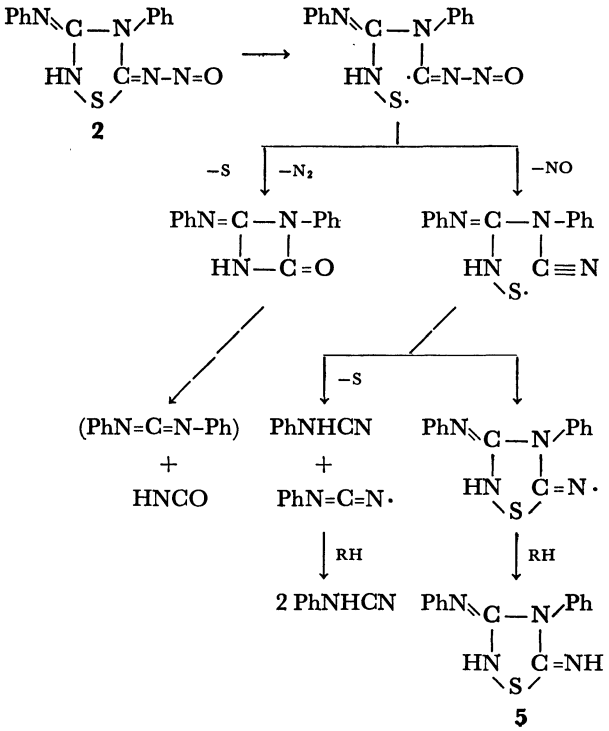
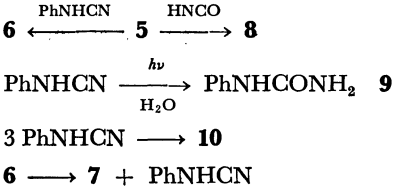


7 9 10

Since the isolation of pure reaction products was difficult, the material balance was not sufficient for quantitative discussion. However, as seen in Table 1, the reaction in a shorter irradiation time gave **5** in a considerable amount and the amount of **6** increased as a reaction time became longer (Runs 1 and 2). Moreover, a shorter irradiation time with a stronger arc gave phenylcyanamide in a fairly good yield (Run 4). Thus, the initial products are **5** and phenylcyanamide and the others are considered to be secondary products. Although **7** is an isomer of **5**, **5** could not be isomerized to **7** by acid or adsorption on silica gel. **9** is the photolysis product of phenylcyanamide with water, being contained in the solvent.

Furthermore, it is shown by experiments using a filter solution that the photolysis of **2** proceeds through π-π^* excitation, similarly to the previous results[2] (see Runs 3 and 4). Therefore, the photolysis is considered to proceed as follows.





Thus, photolysis of **2** is apparently more complicated than that of 2-nitrosoimino-2,3-dihydro-1,3-thiazoles due to the character of the ring.

Experimental

Materials. 4-Methyl-5-nitrosoimino-3-phenyl-1,2,4-thiadiazoline was prepared according to the method of Goerdeler *et al.*,[6] mp 157—158 °C (dec), λ_{max} (C_6H_6): 317.5 (ε 9.08×10^3) and 429 nm (100). 5-Nitrosoimino-4-phenyl-3-phenylimino-1,2,4-thiadiazolidine was prepared from 5-imino-4-phenyl-3-phenylimino-1,2,4-thiadiazolidine according to the Hector's method,[7] mp 183.3 °C (dec), λ_{max} (C_6H_6): 359 (ε 4.0×10^3) and 433 nm (200).

Thermal Decomposition of 4-Methyl-5-nitrosoimino-3-phenyl-1,2,4-thiadiazoline (1). A suspension of 4.0 g (18.1 mmol) of **1** in 200 ml of toluene was refluxed under stirring for 7 hr. After removal of toluene, the residue was chromatographed on silica gel. Elution with benzene-chloroform gave 2.8 g (80%) of 4-methyl-3-phenyl-1,2,4-thiadiazolin-5-one (**3**), mp 76.0—76.5 °C, IR (KBr): 1680 cm^{-1} (C=O).

Found: C, 56.09; H, 4.21; N, 14.43%. Calcd for $C_9H_8N_2OS$: C, 56.23; H, 4.19; N, 14.57%.

Thermal Decomposition of 5-Nitrosoimino-4-phenyl-3-phenylimino-1,2,4-thiadiazolidine (2). The decomposition was carried out qualitatively. A suspension of **2** in xylene was refluxed for 5 hr. After removal of the solvent and addition of petroleum ether to the residue, the resulting crystals were recrystallized from ethanol to give 4-phenyl-3-phenylimino-1,2,4-thiadiazolidin-5-one (**4**) as white needles, mp 165.0—165.3 °C (lit,[8] 162 °C); IR(KBr): 3330 (NH) and 1670 cm^{-1} (C=O). The compound was identical with a sample prepared by nitric acid-catalyzed hydrolysis of 5-imino-4-phenyl-3-phenylimino-1,2,4-thiadiazolidine.

Photolysis of 2. The reactions were carried out under nitrogen.

1) A solution of 1.80 g (6.1 mmol) of **2** in 900 ml of dichloromethane was irradiated through Pyrex filter with a 100 W medium pressure mercury lamp at 20—25 °C for 6 hr, and the solvent was removed. The residue was chromatographed on alumina. Elution with benzene–ether and ether afforded 0.27 g (0.7 mmol, 17.2%) of **6**, mp 192—194 °C (lit,[4] 196—198 °C). IR(KBr): 3480, 3420, 3380, 1660, 1560, and 1535 cm^{-1}; MS: *m/e* 386 (M^+, trace). The spectral data were in agreement with those of an authentic sample[4] (see below).

Elution with ether gave 80 mg (0.3 mmol, 5%) of 5-imino-4-phenyl-3-phenylimino-1,2,4-thiadiazolidine (**5**), mp 179—180 °C (lit,[7] 180—181 °C).

2) A solution of 10.22 g (34.4 mmol) of **2** in 1400 ml of benzene-*N*,*N*-dimethylformamide (DMF) (2 : 1) was irradiated through pyrex filter with the same lamp at 5—10 °C for 40 hr. After the solvent was removed *in vacuo* at 90 °C, the residue was chromatographed on silica gel. Fractions eluted with benzene-dichloromethane (3 : 1—1 : 1) and dichloromethane were evaporated. The residue was dissolved in benzene and addition of hexane gave 1.71 g (4.4 mmol, 19.2%) of **6**, mp 183—185 °C, as precipitates. Fractions eluted with dichloromethane–ether (3 : 1) were evaporat-

ed and rechromatographed on a silica gel dry column with dichloromethane to afford **7** (0.74 g), mp 218—219 °C (from chloroform) (lit,[9] 220—222 °C). Eluate with dichloromethane–ether (1 : 1–1 : 3) was rechromatographed on silica gel to afford 0.26 g of **7** (1.00 g, 3.7 mmol, 10.8% in total) with benzene and chloroform and 0.60 g (1.9 mmol, 11.0%) of **8** with chloroform and ether–ethyl acetate, mp 208—209 °C; IR (KBr): 3480, 3400, 3320 (NH), 1760, 1640, 1610, and 1590 cm^{-1}. The spectral data of **8** were in agreement with those of an authentic sample prepared by another route (see below).

Fractions eluted with acetone and acetone–methanol (1 : 1) were rechromatographed on silica gel. Elution with dichloromethane gave 0.42 g (1.1 mmol, 3.3%) of **11**, mp 201—202 °C (from acetone), and elution with chloroform and ethyl acetate gave 1.02 g of crystalline material. The soluble part in ethyl acetate gave 0.82 g (6.0 mmol, 8.8%) of **9**, mp 148—149 °C (from ethyl acetate) (lit,[10] 148—149 °C). The insoluble part was unidentified.

11 : IR (KBr) : 3420, 3360, 3280, 3100 (NH), 1630, and 1590 cm^{-1}; MS: *m/e* 373 (0.7%), 347 (11), 311 (49), 295 (55), 293 (25), 268 (48), 195 ($PhNHCNPh^+$, 28), 150 (100), 122 (44), 119 (59), and 118 (58). The structure of **11** was unidentified.

3) As a filter solution for 340–360 nm and a coolant, a solution of 490 g of $CoSO_4 \cdot 7H_2O$ and 100 g of $CuSO_4 \cdot 5H_2O$ in 900 ml of water was used.[2] A solution of 6.09 g (20.5 mmol) in 850 ml of benzene–DMF–2-propanol (5 : 7 : 5) was irradiated with the same lamp through the filter solution at 5—10 °C for 20 hr. After evaporation of the solvent, the residue was chromatographed on silica gel. Eluates with benzene–dichloromethane (1 : 1) were treated with dichloromethane and water to afford 0.10 g (0.28 mmol, 2.1%) of **10**, mp 202.5—203.5 °C (lit,[11] 210 °C); IR (KBr): 3330 (NH), 1620, and 1590 cm^{-1}, NMR ($CDCl_3$): δ 5.4 (s, 3H, NH) and 7.35 (s, 15H, Ph); MS: *m/e* 354 (M^+), 236, and 118. Evaporation of the organic layer and washing with dichloromethane gave 0.10 g of **7**. The filtrate was treated with preparative thin layer chromatography (tlc) on silica gel with dichloromethane–ether to give 0.44 g (1.1 mmol, 8.1%) of **6**.

Eluates with benzene–dichloromethane (1 : 1) and dichloromethane were rechromatographed on silica gel. Elution with dichloromethane–ether gave 0.64 g of a mixture, which was separated by preparative tlc with ether to give 20 mg of **7** (in total, 0.12 g, 0.45 mmol, 2.2%). Elution of dichloromethane gave 1.04 g (2.8 mmol. 13.7%) of **11**. Elution of ethyl acetate afforded 0.38 g (2.8 mmol, 6.8%) of **9**.

The products were identified by the melting points and spectral data.

4) A solution of 8.84 g (29.8 mmol) of **2** in 1100 ml of DMF–2-propanol (1 : 1) was irradiated with a 400 W medium-pressure mercury lamp at 10—15 °C using the same filter solution for 3 hr. The UV spectrum of the solution indicated that about 5 mmol of **2** remained unchanged. The solvent was removed below 40 °C *in vacuo* and the residue was chromatographed on silica gel.

Elution with dichloromethane and dichloromethane–ether gave 1.42 g (12 mmol, 20.2%) of phenylcyanamide (identified by IR) and other materials which were rechromatographed on alumina. The fractions eluted with benzene–chloroform (3 : 2—2 : 3) was again chromatographed on silica gel dry column with chloroform to give 90 mg of **6**.

Fractions eluted with dichloromethane–ether and ether were purified by preparative tlc with ethyl acetate–ether to give 0.70 g of **6** (in total, 0.79 g, 2 mmol, 10.1%). Elution with ethyl acetate gave 0.59 g of **9** (4.3 mmol, 7.2%). Other fractions could not be identified.

Preparation of **7**. Ammonia gas was bubbled to 3.0 g (11 mmol) of **5** in 40 ml of ethanol for 2 min and the mixture was heated at 135—140 °C for 3 hr in a sealed tube. After evaporation of the solvent, a small amount of dichloromethane was added to dissolve the residue and ether was added to the solution to precipitate 1.0 g (33%) of **7**, mp 220—221 °C (from ethanol) (lit,[5] 220—222 °C).

Reaction of **5** *and Phenylcyanamide.* A mixture of 5.0 g (18.7 mmol) of **5** and 2.0 g (17 mmol) of phenylcyanamide in 50 ml of chloroform was refluxed for 3 hr. After removal of the solvent, the residue was washed with a small amount of dichloromethane to obtain **6**. The washing was allowed to stand after addition of benzene to precipitate **6**. The total amount was 6.0 g (92%), mp 196—198 °C.

Found: C, 65.09; H, 4.56; N, 21.73; S, 8.10%. Calcd for $C_{21}H_{18}N_6S$: C, 65.25; H, 4.70; N, 21.75; S, 8.29%.

Reaction of **5** *and Cyanic Acid.* A mixture of 3.0 g (11.2 mmol) of **5**, 5 ml of 10% sulfuric acid, and 1.0 g (15.4 mmol) of sodium cyanate was stirred at 120 °C for 20 min to precipitate 2.5 g (72%) of **8**, mp 208—209 °C (from acetone). MS: *m/e* 311 (M^+, 100%), 295 ($M^+ - NH_2$, 16), and 268 ($M^+ - HOCN$, 63).

Found: C, 57.97; H, 4.19; N, 22.51; S, 9.93%. Calcd for $C_{15}H_{13}N_5OS$: C, 57.85; H, 4.22; N, 22.50; S, 10.30%.

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4) K. Akiba, T. Tsuchiya, M. Ochiumi, and N. Inamoto, *Tetrahedron Lett.*, **1975**, 455. Recently, we have investigated the crystal structure of the tri-*p*-bromophenyl derivative of **6** by X-ray diffraction method. From the result, the structure of **6** should be revised as shown in the text, but the revised structure is consistent with the previous experimental results. This result will be reported soon.

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