Anal. Calcd for $C_{26}H_{22}N_4O_4$: C, 68.71; H, 4.88; N, 12.33. Found: C, 68.86; H, 4.99; N, 12.43.

On concentration of the ethereal filtrate 0.4 g (41%) of *N*,*N*-dimethyl-*N'*-phenylurea, mp 134°, was obtained.

Registry No.—**2b**, 29411-17-4; **4b**, 17350-46-8; **4c**, 29411-19-6; **8** (R = Ph), 29411-20-9; **9** (R = Ph), 29520-61-4; *N*,*N*-dimethylformamide, 68-12-2.

Studies of Hydrazine Derivatives. II.[1] The Formation of 1-Phenyl-3-benzoyltriazene by the Base-Catalyzed Condensation of Nitrosobenzene with Benzhydrazide

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Aromatic nitroso compounds are well known to undergo condensation reactions analogous to those of carbonyl compounds. However, nitrosobenzene (**1**) reacted with a monosubstituted or unsymmetrically disubstituted hydrazine to give a triazene *N*-oxide,[2] and attempted triazene formation in reactions of nitroso compounds with hydrazines have been unsuccessful.[3] In this paper we wish to describe the formation of 1-phenyl-3-benzoyltriazene (**2**) by the base-catalyzed condensation of **1** with benzhydrazide (**3**).

Compound **2** has previously been prepared by the reaction of phenylmagnesium bromide with benzoyl azide.[4]

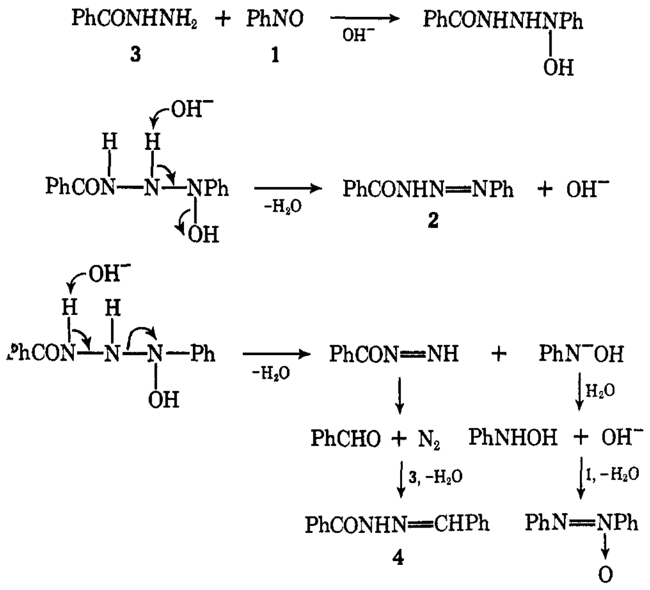
When powdered **1** was added to an aqueous solution of equimolar amounts of **3** and potassium hydroxide at 45–50° with vigorous stirring, a brown oil separated and nitrogen was evolved. After being extracted with ether, compound **2** was separated from the aqueous layer as the silver complex (25%). Benzaldehyde benzoylhydrazone (**4**, 9%), azoxybenzene (24%), benzoic acid (14%), and aniline (4%) were also obtained along with phenyl azide (0.1%) and azobenzene (trace). Either increase or decrease of alkali in the reaction reduced the yield of **2**. Attempted reactions between **1** and **3** in water with sulfuric acid, in *tert*-butyl alcohol with sodium *tert*-butoxide, and in acetic acid did not afford **2** to a significant extent.

As chromatographic treatment on silica gel or alumina brought about the decomposition of **2**, this product could not be obtained quantitatively from the reaction mixture by this technique.

When **2** was treated with dimethylaniline in acetic acid, in hydrochloric acid, or on silica gel in *n*-hexane, *p*-dimethylaminoazobenzene was obtained in 82–84% yield. A diazoaminobenzene-type rearrangement must take place in this process. A solution of the reaction mixture (after being extracted) and dimethylaniline in *n*-hexane was refluxed with a small amount of silica gel for 1 hr and then chromatographed to give *p*-dimethylaminoazobenzene (13%).

The sources of the hydrazone **4** and of azoxybenzene are suggested in Scheme I. Curtius[5] reported that **4** was formed by heating benzhydrazide with alkali, but we were unable to obtain **4** under these conditions in the absence of nitrosobenzene. The formation of aniline was observed by Minato, *et al.*,[6] in the reaction of **1** with hydrazine, though the mechanism has not been well established.

SCHEME I



Experimental Section[7]

Reaction of Nitrosobenzene (1) with Benzhydrazide (3).—To a vigorously stirred solution of 6.8 g (50 mmol) of **3** and 3.2 g (*ca.* 50 mmol) of potassium hydroxide in 75 ml of water was added, over a period of 30 min, 5.4 g (50 mmol) of powdered **1** at 45–50°. The reaction mixture was kept at this temperature for an additional 30 min with stirring. During the reaction, a brown oil separated and gas evolved. The reaction mixture was then cooled, extracted with ether, and separated to an ether layer (a), a water layer (b), and an insoluble solid (c, 1.0 g). The ether layer (a) was washed with aqueous KOH and then with water, dried (Na_2SO_4), and concentrated giving 3.1 g of an oily brown liquid, containing azoxybenzene (2.38 g, 12 mmol, 24%), aniline (0.19 g, 2 mmol, 4%), phenyl azide (0.006 g, 0.05 mmol, 0.1%), and azobenzene (trace), determined by means of column chromatography, vpc, ir, and/or tlc.

The water layer (b), when combined with washings of the ether extract of the reaction mixture, was acidified with dilute hydrochloric acid and extracted with ether. The ethereal solution was washed with water, dried (Na_2SO_4), and concentrated giving 4.6 g of a brown viscous residue (b′), containing benzoic acid (0.86 g, 7 mmol, 14%) as the methyl ester, determined by means of vpc. Addition of an alcoholic solution of silver nitrate to the ethanol solution of b′ caused precipitation of yellow 1-phenyl-3-benzoyltriazenatosilver (4.15 g, 12.5 mmol, 25%); its ir spectrum was identical with that of an authentic sample.[4] Chromatographic treatment of b′ on silica gel or alumina brought about the decomposition of **2**; by the use of a short column (silica

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(1) Part I of this series: S. Ito and T. Narusawa, *Bull. Chem. Soc. Jap.*, **43**, 2257 (1970).

(2) (a) O. Fischer and L. Wacker, *Ber.*, **22**, 622 (1889); (b) E. Bamberger and A. Stiegelmann, *ibid.*, **32**, 3554 (1899); (c) O. Fischer and W. Johannes, *J. Prakt. Chem.*, **92**, 60 (1915).

(3) For a review about reactions of aromatic nitroso compounds, see J. H. Boyer in "The Chemistry of the Nitro and Nitroso Groups," H. Feuer, Ed., Interscience, New York, N. Y., 1969, pp 215–299.

(4) A. Bertho, *J. Prakt. Chem.*, **116**, 101 (1927).

(5) T. Curtius, *Ber.*, **33**, 2560 (1900).

(6) H. Minato and T. Fujisawa, *Bull. Chem. Soc. Jap.*, **39**, 1054 (1966).

(7) Melting points were determined in capillary and are uncorrected. The yields of the products are shown in mole percentage based on **1** or **3** used. For the ir spectroscopic determination, a Nihon-Bunko Model DS-301 spectrometer and a Shimadzu gas chromatograph Model GC-2C for the vpc analysis were employed.

gel), only a small amount of 1-phenyl-3-benzoyltriazene (**2**) was obtained. After recrystallization from *n*-hexane, it melted at 83–84° dec (lit.[4] mp 84° dec). Its ir spectrum was identical with that of an authentic sample.

The ir spectrum of the insoluble solid (c) was identical with that of authentic benzaldehyde benzoylhydrazone (**4**); recrystallization of c from methanol gave **4**, mp 204–205° (lit. mp 204–205°). When c was considered pure, the yield of **4** was 4.5 mmol (9%).

Registry No.—**1**, 586-96-9; **2**, 29411-28-7; **3**, 613-94-5.

The Cyclization Reaction of Alkylthiomercaptoenethioamide with Carbonyl Compounds

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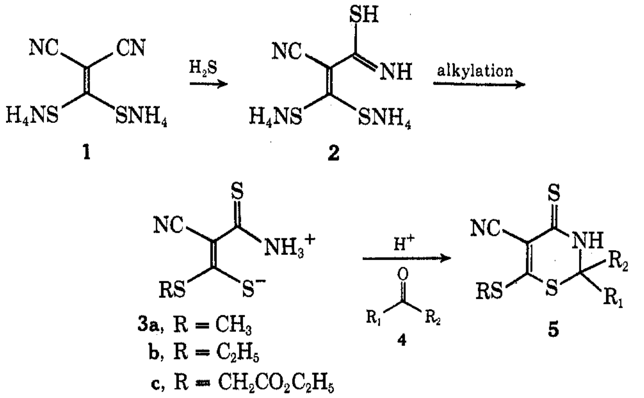
In the course of the investigation of the behavior of enedithiol compounds,[1,2] the reaction of the alkylthiomercaptoenethioamide compound has been studied.

It has been found that 2,2-disubstituted 5-cyano-6-alkylthio-2,3-dihydro-4*H*-1,3-thiazine-4-thione (**5**) type compounds could be isolated from the reaction of an alkylthiomercaptoenethioamide, such as 3-alkylthio-3-mercapto-2-cyanothioacrylamide (**3**), with a variety of carbonyl compounds in acidic medium. The derivatives of 4*H*-1,3-thiazine-4-thione have heretofore not been isolated, although there have been many reports on the preparation of 2*H*-1,3-thiazine-2-thione derivatives[3-6] and 6*H*-1,3-thiazine-6-thione derivatives.[7-10]



Compound **3** was obtained from bisammonium 2,2-dicyanoethenedithiol (**1**) with hydrogen sulfide followed by alkylation of the intermediate 3,3-bis(ammoniumthio)-2-cyanothioacrylamide (**2**). A zwitterion structure was assigned to compound **3a** on the basis of the nmr spectrum (a broad peak at δ 5.00 is characteristic for NH_3^+ group). Compound **5** was obtained in the form of yellow crystals from the reaction of compound **3** and a carbonyl compound **4** by refluxing in alcohol in the presence of sulfuric acid. The physical data of the new compounds are summarized in Table I.

The structure of 2,2-disubstituted 5-cyano-6-alkylthio-2,3-dihydro-4*H*-1,3-thiazine-4-thione was established on the basis of spectroscopic evidence together with elemental analyses (see Table II). Thus the ir spectrum revealed the presence of an amino (3120 cm^{-1}) and conjugated cyano (2210 cm^{-1}) group. The nmr spectrum showed the presence of an NH group (a broad peak at *ca.* δ 10.60). The presence of NH was also seen by its effect on the neighboring proton of the R_1 group, causing a split (J = *ca.* 1 Hz). The mass spectrum of **5** showed a characteristic fragment at the mass number of 126, which was considered to be a fragment of the ($M - SR - NHR_1R_2$) ion (see Table III). The uv spectrum of **5** showed several characteristic absorptions (see Table IV).

Compounds **5** synthesized by the present method were 5-cyano-6-methylthio-2,3-dihydro-4*H*-1,3-thiazine-4-thione-2-spirocyclohexane (**5a**), 2,2-dimethyl-5-cyano-6-methylthio-2,3-dihydro-4*H*-1,3-thiazine-4-thione (**5b**), 2-methyl-5-cyano-6-methylthio-2,3-dihydro-4*H*-1,3-thiazine-4-thione (**5c**), 2-phenyl-5-cyano-6-methylthio-2,3-dihydro-4*H*-1,3-thiazine-4-thione (**5d**), 2-furyl-5-cyano-6-methylthio-2,3-dihydro-4*H*-1,3-thiazine-4-thione (**5e**), 5-cyano-6-ethylthio-2,3-dihydro-4*H*-1,3-thiazine-4-thione-2-spirocyclopentane (**5f**), 2-ethyl-2-methyl-5-cyano-6-ethylthio-2,3-dihydro-4*H*-1,3-thiazine-4-thione (**5g**), 2-(3′,4′-methylenedioxyphenyl)-5-cyano-6-ethylthio-2,3-dihydro-4*H*-1,3-thiazine-4-thione (**5h**), and 2,2-dimethyl-5-cyano-6-ethoxycarbonylmethylthio-2,3-dihydro-4*H*-1,3-thiazine-4-thione (**5i**), respectively.

Experimental Section

3-Methylthio-3-mercapto-2-cyanothioacrylamide (**3a**).—Compound **2** was prepared by our method.[11] To the mixture of **2** (17 g, 0.08 mol), sodium hydroxide (6.4 g, 0.16 mol) in water (50 ml), and methanol (50 ml) was added dropwise dimethyl sulfate (7.3 ml, 0.08 mol) under cooling (ice water) and stirring. The reaction mixture was allowed to stand in an icebox for 3 hr. A small amount of solid product was filtered off. It was considered to be 3,3-dimethylthio-2-cyanothioacrylamide by comparison of its ir spectrum with that of the authentic specimen.[11] The yellow filtrate was mixed with 500 ml of water. To the above solution was added 30 ml of concentrated hydrochloric acid. The crude material was filtered, washed with diluted hydrochloric acid, dried in vacuum desiccator for 20 hr, and recrystallized from methanol as yellow needles: yield 15 g, 98%; mp 140–141°; ir (KBr) 3280 (s, NH_3^+), 2200 (vs, conjugated CN), 1593 cm^{-1} (vs, conjugated C=C); nmr (DMSO-d_6) δ 5.00 (br, 3, NH_3^+), 2.48 (s, 3, CH_3); uv $\lambda_{\max}^{99\%\ \mathrm{EtOH}}$ 246, 286, 341 mμ (log ε 3.60, 3.72, 4.13). *Anal.* Calcd for $C_5H_6N_2S_3$: C, 31.57; H, 3.15; N, 14.72; S, 50.56; mol wt, 190.23. Found: C, 31.68; H, 3.18; N, 14.66; S, 50.60; mol wt, 186 (vapor pressure osmometer, in acetone).

3-Ethylthio-3-mercapto-2-cyanothioacrylamide (**3b**).—The ethylation of **2** was worked up with diethyl sulfate as mentioned in preparation of **3a**. The resulting yellow material was recrystallized from methanol as yellow needles: yield 94%; mp 149–

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