pale yellow needles; mp 125–126°; ir (Nujol) 686 s, 740 vs, 794 m, 833 w, 848 m, 918 m, 1002 m, 1022 m, 1105 vs, 1160 s, 1176 s, 1486 m, 1587 w (C=C aromatic) and 1733 cm^{-1} (C=O); nmr ($CDCl_3$) δ 7.35 ppm (m).

Anal. Calcd for $C_{21}H_{15}O_6P$: C, 63.96; H, 3.85; P, 7.86. Found: C, 63.48; H, 4.14; P, 7.67.

III is soluble in benzene and in warm methanol and insoluble in water or carbon tetrachloride.

The mother liquor from the recrystallization of III was concentrated to low volume, filtered, and evaporated to dryness, giving 7.05 g (22%) of pale yellow, crystalline solid, mp 70–72°, identified by its ir spectrum as impure diphenyl carbonate. The melting point was raised to 76.5–77.5° (lit.[36] mp 79°) by recrystallization from methanol–water.

Anal. Calcd for $C_{13}H_{10}O_3$: C, 72.89; H, 4.71. Found: C, 71.43; H, 4.56; P, 0.86.

The phenyl chloroformate used in this reaction did not contain any diphenyl carbonate (ir). The diphenyl carbonate is therefore a by-product of the reaction with Na_3P.

Basicity Measurements.—The base strengths of I and II were determined by the MeOD method,[28] using 0.5 mm cells and a grating instrument (Perkin-Elmer 421) calibrated with polystyrene. The spectra were scanned from 2800 to 2200 cm^{-1}. A 0.25 *M* solution of MeOD in CCl_4 showed a strong, sharp peak at 2680 cm^{-1} (ν_{OD} free) and a strong, broad peak at 2482 cm^{-1} (ν_{OD} bonded, owing to self-association of the MeOD). Upon the addition of a base (1.0 *M*), the 2680-cm^{-1} peak diminished in intensity and the 2482-cm^{-1} peak shifted and became stronger. Observed shifts for various bases, relative to the 2680-cm^{-1} peak, were $\Delta\nu$ 120 (DMF), 100 (dioxane, lit.[28] 111), 65 (CH_3CN, lit.[28] 63), 35 (I), and 40 cm^{-1} (II).

Using the data, and the expression $pK_a = 0.1[\Delta\nu] - 14.4$ derived from Arnett's Figure 5,[28] the base strengths of I and II were calculated to be $pK_a = -10.9$ and -10.4, respectively.

The phenyl ester III was not sufficiently soluble in CCl_4 to obtain a measurement.

Registry No.—I, 31081-90-0; II, 31128-88-8; III, 31128-89-9.

Acknowledtments.—We are indebted to Dr. R. H. Dinius, Auburn University, for the ^{31}P nmr spectra, and to Mr. G. J. Boudreaux and Miss E. R. McCall of this Laboratory for the ^1H nmr spectra and ir basicity measurements, respectively.

(36) P. D. Ritchie, *J. Chem. Soc.*, 1054 (1935).

Photolysis and Pyrolysis of 2-Azido-3-nitronaphthalene

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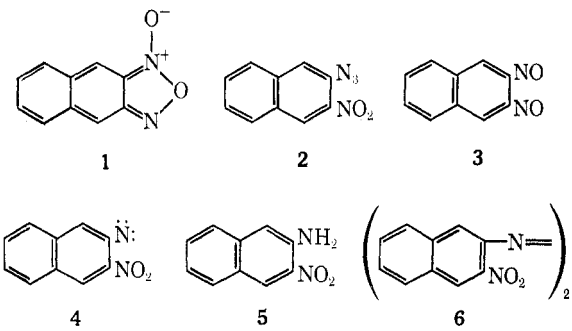
To test the formation of an apparently unfavorable quinonoid system contained in naphtho[2,3-*c*]furoxan (**1**), the expulsion of nitrogen from 2-azido-3-nitronaphthalene (**2**) has been investigated.[1,2] As expected, both irradiation and heat bring about the release of molecular nitrogen; however, neither the furoxan nor its isomer, 2,3-dinitrosonaphthalene (**3**), could be detected.

Consideration of the greater thermal stability of 5-nitro- and 8-nitro-2-azidonaphthalene[3] over 1-nitro-2-azidonaphthalene and the isomer **2** provides an explanation for an increased facility in the release of nitrogen from **2** through anchimeric assistance by the adjacent nitro group. In the present instance, no products in which a new NO bond is formed were isolated. The reaction apparently leads to the intermediate 3-nitronapthyl-2-nitrene (**4**). Hydrogen abstraction from the solvent with the formation of 2-amino-3-nitronaphthalene (**5**) in both thermal and photoelimination reactions is diagnostic of the nitrene intermediate. The additional photogeneration of 3,3′-dinitro-2,2′-azonaphthalene (**6**) is best accounted for by interaction between the azide **2** and the nitrene **4**.



1 **2** **3**

4 **5** **6**

Experimental Section[4]

After nitrogen was flushed through a solution of the azide **2** (200 mg, 0.93 mmol) in anhydrous benzene for 16 hr, it was irradiated with 254-nm low-pressure mercury lamps in a Rayonet chamber reactor and the reaction was monitored by ir. After 1.5 hr of irradiation the solution was concentrated under vacuum (60°). The residue was triturated with benzene (10 ml), filtered, and twice recrystallized from nitromethane as red needles of 2,2′-dinitroazonaphthalene (33 mg, 18.5%): mp 365–370° dec; ν max (KBr) 1520 and 1340 cm^{-1} (NO_2); mass spectrum *m/e* 372 (M^+, parent peak), 356 $(M - O)^+$, 340 $(M - O_2)^+$, 310 $(M - NO_2 - O)^+$, 200 $(M - C_{10}H_6NO_2)^+$, 144 $(C_9H_6NO)^+$, 114 $(C_9H_6)^+$, and 57 $(C_9H_6)^{2+}$; λ_{max} ($CHCl_3$) 290 nm (ϵ 38,370) and 390 (17,740).

Anal. Calcd for $C_{20}H_{12}N_4O_4$: C, 64.52; H, 3.22; N, 15.06; mol wt, 372. Found: C, 64.46; H, 3.18; N, 15.27.

The benzene filtrate was concentrated and the residual solid was purified by chromatography over a column of silica gel (10 × 1 in.). Elutions with a 1:1 hexane–benzene mixture (450 ml) gave 2-azido-3-nitronaphthalene (6 mg, 3%), mp and mmp (with an authentic sample) 101–102°. Subsequent elutions with the same solvent mixture (600 ml) and a 1:2 mixture (300 ml) gave a red residue. It was treated with Norit in benzene and recrystallized from hexane as microscopic red needles of 2-amino-3-nitronaphthalene (8.5 mg, 4.5%): mp and mmp (with the authentic sample) 108–109°; ir (KBr) superposable with the authentic spectrum. Further elutions with polar solvents afforded an intractable resinous product.

A solution of the azide (200 mg, 0.94 mmol) in anhydrous octane (10 ml) was heated at 100° with stirring for 8 hr while the reaction was monitored by tlc. From the dark reaction mixture the solvent was removed under vacuum [50° (25 mm)]. The residue upon tlc examination, using ChromAR-500 sheets with benzene and ethyl acetate solvents, indicated the presence of the unreacted 2-azido-3-nitronaphthalene and 2-amino-3-nitronaphthalene. The residue was purified by chromatography

(1) A. Rahman, A. J. Boulton, D. P. Clifford, and G. J. T. Tiddy, *J. Chem. Soc. B*, 1516 (1968), reported stability of the azide **2** which is inconsistent with the present observations.

(2) The azide was prepared from 2,3-dinitronaphthalene.[1] A sample of this dinitro derivative was obtained from the Fundamental Research Company, Berkeley, Calif.

(3) M. O. Forster and H. E. Fierz, *J. Chem. Soc.*, **91**, 1942 (1907), reported 5-nitro-2-azidonaphthalene, mp 133.5° (no decomposition) and stability in boiling glacial acetic acid; 8-nitro-2-azidonaphthalene, mp 108° (no decomposition); 1-nitro-2-azidonaphthalene, mp 116–117° (vigorous decomposition) and slow evolution of nitrogen when heated in ethanol.

(4) Microanalyses by Micro-Tech Laboratories, Skokie, Ill. Instrumental data were obtained from a Perkin-Elmer 237-B infrared spectrophotometer, a Cary-14 ultraviolet spectrometer, a Perkin-Elmer 270 mass spectrometer, a Varian Aerograph 1800 gas chromatograph, and a Reichert microscope melting point apparatus.

over silica gel (12 × 1 in.). A 1:1 mixture of hexane–benzene (33 ml) eluted 2.2 mg of a pink residue which was found to contain, by gc (5% SE-30)–mass spectral analysis, four volatile fractions with molecular ions m/e 139, 226 ($C_{16}H_{34}$),[5] 173 ($C_{10}H_7NO_2$),[6] and 253 (probably $C_{18}H_{23}N$) in their order of appearance. A mixture of hexane–benzene (1:2, 400 ml) eluted 2-azido-3-nitronaphthalene (55 mg, 28%): mp and mmp (with the authentic sample) 101–102°; ir (CH_2Cl_2) superposable with that of the authentic material. A 1:3 mixture of the same solvents (600 ml) eluted 2-amino-3-nitronaphthalene (3.8 mg, 3.9%). Gc analysis over a 3% SE-30 column (6 ft × 1/8 in., at 200°, Varian-1800 gas chromatograph) confirmed the presence of 2-amino-3-nitronaphthalene associated with trace amounts of an unidentified impurity. Further elutions with chloroform and a chloroform–ethanol mixture (9:1) gave a dark intractable solid which charred upon vacuum sublimation.

Registry No.—**2**, 22496-30-6; **5**, 13115-28-1; **6**, 31417-80-8.

(5) Assumed to be a combination of solvent radicals.
(6) Assumed to be β-nitronaphthalene.

The Reaction of Dithiazolium Cations with Sodium Azide

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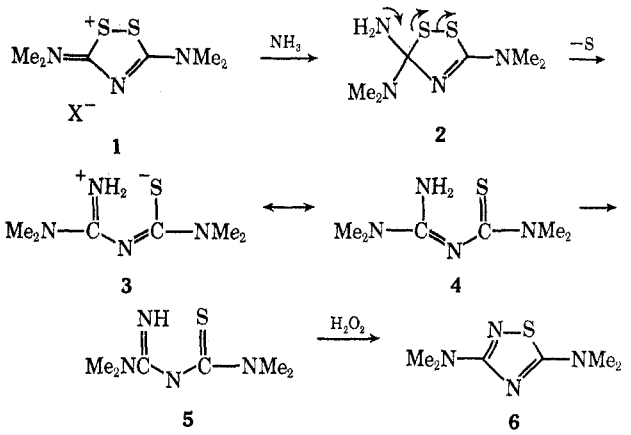
3,5-Bis(dimethylamino)-1,2,4-dithiazolium chloride (**1**, X = Cl) and a number of closely related dithiazolium salts are chemosterilants against house flies (*Musca domestica* L.).[1] To see whether similar biological activity might be found in geometrically similar, uncharged heterocyclic compounds, we wished to prepare a series of bis(dimethylamino) heterocyclic compounds including the 1,2,4-thiadiazole **6**. Various syntheses of amino-1,2,4-thiadiazoles have been developed,[2] but many of them give only mono- or unsubstituted amino groups. 3,5-Diamino-1,2,4-thiadiazoles can be prepared by oxidation of amidinothioureas,[2,3] and, since amidinothioureas can be made by reacting iminodithiazolidine salts and amines,[3] we were able to prepare **6** from **1** as shown in Scheme I. The overall yield of **6** was about 25%.[1b] The probable mechanism[3,4] of the addition of ammonia presumably involves ring opening and extrusion of elemental sulfur, assisted by an electron pair from either the amino or dimethylamino group of **2**.

The immediate species after loss of sulfur is interesting. Resonance form **3** suggests that the remaining sulfur should be rather nucleophilic, and we reasoned that, if the ring opening were initiated by a nucleophile that contained an inherent electrophilic center, direct cyclization might occur. To test this hypothesis we reacted **1** with sodium azide (NaN_3).

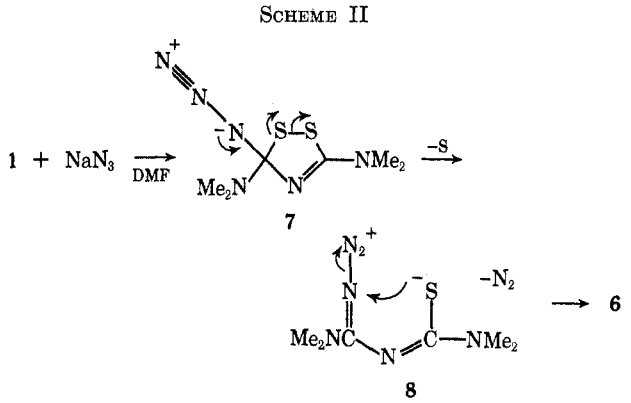
When **1** and NaN_3 were heated together in water, no reaction occurred. However, in dimethylformamide

SCHEME I



(DMF), an intense blue color quickly developed, and at about 80° nitrogen was evolved. In a few minutes the color was discharged, and the product, obtained in 75% yield after distillation, was the same 1,2,4-thiadiazole prepared earlier. The rationale is shown in Scheme II.

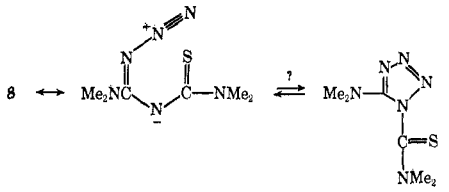
SCHEME II



The N_2^+ end of the azide function evidently creates the desired electrophilic center and also serves as a good leaving group.[5]

3,5-Dipiperidino-1,2,4-dithiazolium bromide reacted analogously with NaN_3 to give a good yield of 3,5-dipiperidino-1,2,4-thiadiazole. We then tried the reaction on an unsymmetrically substituted dithiazolium salt and chose the dimethylaminomorpholino compound **9,9′** with the hope that the rather large difference in basicity[6] between dimethylamine (pK_B = 3.36) and morpholine (5.64) might result in selective nucleophilic attack at one of the two ring carbons. Although **9,9′** was somewhat less reactive than **1**, it did react smoothly

(1) (a) R. L. Fye, G. C. LaBrecque, A. B. Bořkovec, and J. Morgan, Jr., *J. Econ. Entomol.* **62**, 522 (1969); (b) J. Oliver, S. C. Chang, R. T. Brown, J. B. Stokes, and A. B. Bořkovec, unpublished results.
(2) F. Kurzer, *Advan. Heterocycl. Chem.*, **5**, 119 (1965).
(3) (a) S. N. Dixit, *J. Indian Chem. Soc.*, **37**, 151 (1960); (b) *ibid.*, **38**, 221 (1961).
(4) Nucleophilic additions to the closely related 1,2-dithiolium cations have been studied in some detail. For a review see H. Prinzbach and E. Futterer, *Advan. Heterocycl. Chem.*, **7**, 39 (1966).
(5) The editor has pointed out that intermediate **8** is very similar to the proposed intermediates in the thermal isomerizations of 5-aminotetrazoles: R. A. Henry, W. G. Finnegan, and E. Lieber, *J. Amer. Chem. Soc.*, **76**, 88 (1954); **77**, 2264 (1955). Thus **8** could possibly have closed to a thiocarbamoyltetrazole. We have no evidence that such a reaction occurred; however, the isolated thiadiazoles were usually much more soluble than most tetrazoles, and small amounts of the latter could have escaped detection.



(6) H. K. Hall, *ibid.*, **79**, 5441 (1957).