water to give orange crystals (85 mg). Two recrystallizations from Skellysolve C gave orange crystals of the azo sulfide **4a**: mp 143.5–145° (lit.[4] mp 140–141°); uv max 424 mμ (ε 782), 418 (765), 310 (4355), 240 (14,800).

A quantitative yield of azo sulfide was obtained when air was bubbled through a methanolic solution of **3a** containing a trace of sodium hydroxide.

B.—A solution of the azoxy sulfide **2a** (250 mg) in dry ether was stirred with lithium aluminum hydride (210 mg) for 1 hr while the reaction mixture was cooled in an ice bath. The light green solution was decomposed in the usual manner and gave a crude product containing yellow and white crystals. The crude product was oxidized with phenyliodoso acetate in acetic acid to give an orange solid (228 mg), mp 131–136°. This was recrystallized from Skellysolve C to give pure **4a**.

Prepartion of the Hydrazo Sulfoxide 3b.—Zinc dust (2.5 g) was added in several portions over a 2–3-min period to a solution of the azoxy sulfoxide **2b** (800 mg) in acetic acid (50 ml) while the reaction mixture ws agitated at 50–55°. The reaction mixture was stirred for an additional 10 min and was filtered. The crude product was precipitated from ice water and was recrystallized three times from methanol to afford white needles of the hydrazo sulfoxide (650 mg), mp 188–189° dec.

Anal. Calcd for $C_{12}H_{10}ON_2S$: C, 62.60; H, 4.38; N, 12.16; S, 13.91. Found: C, 62.50; H, 4.00; N, 12.00; S, 13.64.

Although **3b** is stable in the solid state or in a methanolic solution, an acetic acid solution of **3b** is rapidly oxidized by air to give brown tar. In acetone solution **3b** (30 mg) and excess potassium permanganate solution gave the expected azoxy sulfone[6,12] (**2**, X = SO_2).

Preparation on Azo Sulfoxide 4b. A.—An aqueous solution (10 ml) of ferric chloride (1.5 g) was added at room temperature to a solution of hydrazo sulfoxide **3b** (253 mg) in methanol (40 ml). Additional methanol was added dropwise to remove the resulting cloudiness. The solution was set aside at room temperature for 2 hr, and then diluted with ice water (150 ml) and cooled overnight in a refrigerator to give orange needles (230 mg), mp 135° dec. A metal spatula was blackened when dipped in a hot methanolic or Skellysolve B solution of this compound. Recrystallization from Skellysolve B gave orange needles of the azo sulfoxide **4b**: mp 138° dec; uv max 306 mμ (ε 2000), 232 (18,700).

Anal. Calcd for $C_{12}H_8ON_2S$: C, 63.14; H, 3.53; N, 12.28; S, 14.05. Found: C, 62.69; H, 3.68; N, 11.34; S, 14.31.

The filtrates from the recrystallization of **4b** gave light yellow crystals of benzocinnoline, mp and mmp 153–156°. Authentic benzocinnoline, mp 156°, was prepared according to Badger, *et al.*[17]

B.—A mixture of hydrazo sulfoxide **3b** (100 mg), PBA (0.219 *M*, 3 ml), and chloroform (10 ml) was shaken for 2 min before being quenched with 5% sodium hydroxide solution (5 ml). The chloroform solution was worked up in a usual way to afford **4b** (85 mg), mp 137° dec.

Oxidation of Azo Sulfide 4a with PBA.—A solution containing azo sulfide **4a** (400 mg), a calculated amount of 0.335 *M* PBA, and chloroform (20 ml) was set aside for 2 days at room temperature. The products were worked up in the usual manner. One molar equivalent of PBA gave **2b**, **4b**, **4a**, and benzocinnoline; 2 molar equiv of PBA gave **2b** (59%), benzocinnoline (15%), and benzocinnoline *N*-oxide (10%); 2.5 molar equiv of PBA gave **2b** (75%) and benzocinnoline *N*-oxide (6%).

Benzocinnoline *N*-oxide was compared with an authentic sample prepared according to the method of King and King,[18] mp and mmp 135–137°.

Dethionylation of 2b.—A solution of 650 mg of **2b** in 7 ml of concentrated sulfuric acid was heated at 100° for 40 min and then poured on ice. The dark, insoluble product (350 mg) was given a charcoal treatment in benzene, and 100 mg (19%) of white, crystalline benzocinnoline *N*-oxide, mp 135–137°, was isolated. The acidic filtrate was neutralized with 6 *N* sodium hydroxide and a pale yellow precipitate, 210 mg (44%), was collected and identified as benzocinnoline.

Registry No.—**2b**, 30338-26-2; **3b**, 30388-27-3; **4b**, 30117-56-7.

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(18) F. E. King and T. J. King, *ibid.*, **825** (1945).

Derivatives of Dibenzo[*b*,*f*][1,4,5]thiadiazepine. VI.[1] Nitro and Amino Compounds

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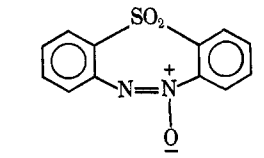
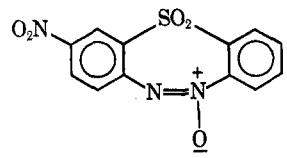
In previous papers of this series the ring-substituted derivatives of dibenzo[*b*,*f*][1,4,5]thiadiazepine were prepared by the ring closure of appropriately substituted diphenyl sulfides or sulfones. This paper presents the results of the nitration of the azoxy sulfone **1** and the chemistry of the resulting mono- and dinitro compounds.

Although the successful nitration of various acyclic azobenzenes is described in the literature,[4,5] the application of this reaction to the azo sulfone **5** (R = H)



1



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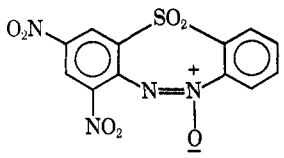

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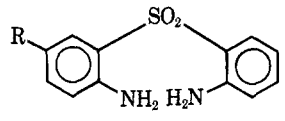

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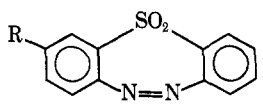

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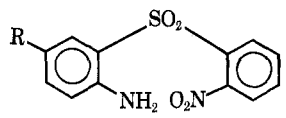
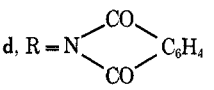


6

a, R = NH_2
b, R = $NHCOCH_3$
c, R = $NHSO_2C_6H_5$



d

gave extensive tar formation even under the mildest conditions that were attempted. On the other hand, the nitration of the azoxy sulfone **1** gave the mono- and dinitro products, which are deduced to be the 9-nitrodibenzo[*b*,*f*][1,4,5]thiadiazepine 5,11,11-trioxide (**2**) and the corresponding 7,9-dinitro derivative (**3**), respectively. The choice of rings in the electrophilic substitution follows from the known behavior of azoxybenzenes,[6-8] and the assignment of the position is

(1) For paper V, see H. H. Szmant and Y. L. Chow, *J. Org. Chem.*, **36**, 2887 (1971).

(2) Department of Chemistry, University of Detroit, Detroit, Mich. 48221.

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(4) J. Werner and E. Stiasny, *Ber.*, **32**, 3256 (1899).

(5) J. Burns, H. McCombie, and M. Scarborough, *J. Chem. Soc.*, 2928 (1928).

(6) L. C. Behr, *J. Amer. Chem. Soc.*, **76**, 3672 (1954).

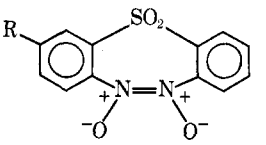
(7) T. Ukai and Y. Ito, *J. Pharm. Soc. Jap.*, **3**, 821 (1953).

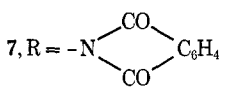
(8) K. H. Schündehütte in "Methoden der Organischen Chemie," Vol. 10, 4th ed, part 3, G. Thieme Verlag, Stuttgart, 1965, p 745.

based on evidence presented below. In an attempt to prove the structure of the mononitro compound **2** it was subjected to mild reduction, but it was found impossible to reduce the nitro group without, at the same time, affecting the azoxy function. The use of stannous chloride converted **2** to 2,2′-5-triaminodiphenyl sulfone (**4a**), and the 5-amino group of this compound was found to be selectively acetylated and benzenesulfonated to give **4b** and **4c**, respectively. The treatment of **2** with the complex of hydrogen sulfide and piperidine, followed by air oxidation, afforded 9-aminodibenzo[*b*,*f*][1,4,5]thiadiazepine 11,11-dioxide (**5a**). Presumably this method of reduction gives the intermediate amino hydrazo compound, and the latter is then oxidized to the azo compound **5a**. Our failure to bring about the selective reduction of the nitro group by means of the hydrogen sulfide–amine complex must be contrasted with the successful application of such a reagent in the case of *p*,*p*′-dinitroazoxybenzene[8] and points to the greater vulnerability of our *cis*-azoxy function to reduction as compared to the *trans*-azoxy system present in the acyclic examples. The facile reduction of the azoxy group in this heterocycle has been previously noted.[9,10]

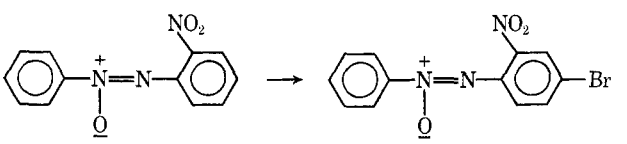
In order to prove the identity of **4a** and **5a** and, simultaneously, to investigate an alternative synthetic route leading to **5a**, use was made of the condensation capability of *p*-benzoquinone diimide derivatives.[11,12] The addition of *o*-nitrobenzenesulfinic acid to *N*,*N*′-bis(dimethylaminosulfonyl)-*p*-benzoquinone diimide,[13] followed by the easy hydrolytic removal of the dimethylaminosulfonyl groups, gave a direct synthesis of 2,5-diamino-2′-nitrodiphenyl sulfone (**6a**). The latter was also prepared starting from *o*-nitrothiophenol and *p*-benzoquinone dibenzimide.[11,12] The 5-amino group of **6a** was selectively benzenesulfonated, acetylated, and converted to the phthalimide (**6b–d**), and the reduction of **6a** and **6c** gave **4a** and **4c**, respectively, identical with the samples of **4a** and **4c** obtained by the reduction of the nitro azoxy compound **2**. This identity proves that the nitration of **1** occurs para to the nitrogen bridge. Compounds **6a–d** are sensitive to moderately strong basic conditions, as may well be expected because of the favorable structure for the occurrence of the Smiles rearrangement.[14,15] It is interesting to note that **6a** is unexpectedly a red crystalline solid, while its hydrochloride is colorless and the substitution products **6b–d** are pale yellow. The presence of the deep color in **6a** suggests the formation of charge-transfer self-complexes similar to those observed in the case of α-aminophenyl-ω-nitrophenylalkanes.[16]

Oxidative cyclization of **6b** and **6c** with peracids or phenyliodoso diacetate gave only amorphous polymeric products, presumably because of the facile oxidation of the monosubstituted *p*-phenylenediamine moiety to the reactive[11] *p*-quinone diimide system. However, the phthalimide derivative **6d** was successfully converted to the cyclic azo system **5d**, by means of phenyliodoso diacetate, and the latter gave, upon treatment with hydrazine, the amino azo compound **5a** identical with that obtained by the above-mentioned reduction of **2**, the nitration product of the azoxy heterocycle **1**. The oxidation of the phthalimido azo compound **5d** with peracetic acid gave a product containing two additional oxygen atoms per molecule, the elementary composition of which agrees with that of an azodioxy derivative (**7**). The latter structure





was suggested[17] for the dimer of nitroso compounds. The structure of the dinitro compound **3** is deduced from the observation[8] that electrophilic substitution in 2-nitroazoxybenzene (**8**) gives **9**; *i.e.*, it occurs in



8 **9**

the benzene ring adjoining the oxygen-free nitrogen even in the presence of a nitro group. The reduction of **3** by means of stannous chloride to the tetraamino sulfone followed by a mild acetylation gave only a diacetyl derivative (**10**), again reflecting the steric hindrance of the amino groups ortho to the sulfone function.

Experimental Section[18]

Nitration of 1.—A mixture of concentrated nitric acid (10 ml) and concentrated sulfuric acid (5 ml) was added dropwise over 2 hr to a cold solution of **1** (1 g) in concentrated sulfuric acid. The reaction mixture was stirred in an ice bath for 10 additional hr and was then poured into ice water. The precipitate was filtered, washed with water and cold methanol, dried, and dissolved in benzene. The benzene solution was treated with charcoal and fractionally crystallized to afford light yellow cubes (725 mg) and yellow needles (290 mg). The cubes were recrystallized four times from benzene to afford **2**, mp 272–273° dec. The yellow needles were recrystallized three times from benzene to give **3**, mp 248–249°.

Although the dinitro compound **3** was recovered unchanged on refluxing in an acetic acid solution for 2 days or upon treatment with concentrated sulfuric acid at 50°, **3** was extensively decomposed in dilute sodium hydroxide solution and even on an alumina column.

Reduction of 2. A.—The powdered nitro compound **2** (1.2 g) was added to a solution of stannous chloride (6 g) in concentrated hydrochloric acid. The reaction mixture was heated for 35 min and then cooled to give a white precipitate. This precipitate was taken up in hot water and treated with sodium hydroxide solution (10%) to give the free amine. The free amine was recrystallized from benzene–methanol to afford pale yellow cubes of **4a**, mp 167–168°. The monoacetyl derivative **4b**, mp 176–177°, was

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(10) N. L. Allinger and G. A. Youngdale, *J. Amer. Chem. Soc.*, **84**, 1020 (1962).
(11) R. Adams and J. L. Anderson, *ibid.*, **72**, 5154 (1950).
(12) R. Adams, E. F. Elslager, and T. E. Young, *ibid.*, **75**, 663 (1953).
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(14) M. F. Grundon and B. T. Johnston, *J. Chem. Soc. B*, 255 (1966).
(15) J. F. Bunnett and R. E. Zahler, *Chem. Rev.*, **49**, 273 (1951).
(16) R. L. Hansen and F. F. Neumayer, *J. Phys. Chem.*, **71**, 3047 (1967).
(17) B. G. Gowenlock and W. Luttke, *Quart. Rev., Chem. Soc.*, **12**, 321 (1958).
(18) Satisfactory analytical values (±0.3% for C, H, N, and S) were reported for compounds **2**, **4a**, **4c**, **5a**, **5d**, **6a**, **6c**, **6d**, **7**, and **10**. N and S values were reported for **4b**; C values found for **3** and **4d** were 0.45% high and 0.41% low, respectively.

prepared by means of acetic anhydride in the presence of 1 *M* hydrochloric acid and was recrystallized from benzene–methanol. The monobenzenesulfonyl derivative **4c**, mp 214–216°, was recrystallized from methanol.

B.—A solution of **2** (550 mg) in pyridine (50 ml) was stirred and cooled in an ice bath. A mixture of piperidine (2 g) and pyridine (20 ml) was saturated with H_2S to give a precipitate, which was added to the former solution. The reaction mixture was stirred for 6 hr to give a dark red solution. The bulk of solvent was removed under vacuum and the residue was diluted with water (350 ml). The precipitate was taken up in methanol (150 ml) and the filtered solution was aerated overnight in the presence of a few drops of sodium hydroxide solution (10%). The mixture was diluted with water to give a red solid (230 mg), which was extracted with cold 20% hydrochloric acid. The free base was liberated by addition of aqueous sodium hydroxide and was recrystallized from methanol to give orange crystals of **5a**, mp 271–273° (transition to red crystals at 250°). The orange-colored phthalyl derivative **5d**, mp 305–306°, was prepared by heating **5a** with phthalic anhydride in acetic acid and was recrystallized from acetic acid.

Synthesis of 6. A.—*N*,*N*′-Bis(dimethylaminosulfonyl-*p*-benzoquinonediimide) was prepared from bis(dimethylsulfonyl-*p*-phenylenediamine).[18] The crude bisdiimide, 10.4 g, was added in several portions to a solution of *o*-nitrobenzenesulfinic acid[19] (7.7 g) in glacial acetic acid (156 ml) containing 8 drops of sulfuric acid. The reaction mixture was stirred overnight and then poured into water. The precipitate was collected on a cooled Büchner funnel. This precipitate was treated with hydrogen peroxide (30%, 5 ml) in acetic acid for 0.5 hr and reprecipitated again by pouring into water. The precipitate was refluxed in concentrated hydrobromic acid (50 ml) for 10 min. The resulting solution was diluted with water to 600 ml and was treated with charcoal. The filtrate was neutralized with 10% sodium hydroxide solution to give a dark red solid. Recrystallization from methanol gave red needles of **6a** (4.65 g, mp 143–144°). The monobenzenesulfonyl derivative **6c**, mp 144–146°, was recrystallized from methanol.

A solution of **6a** (1.82 g), phthalic anhydride (940 mg), and glacial acetic acid (50 ml) was kept at room temperature overnight and then at 60° for 10 hr. The precipitate (2.6 g) was recrystallized to afford the yellow monophthalyl derivative **6d**, mp 289–292°.

The red needles of **6a** dissolved in dilute hydrochloric acid to give a colorless solution from which white needles of the hydrochloride, mp 148–153°, were obtained. The free base is regenerated with 10% aqueous sodium hydroxide solution.

B.—Alternatively, **6a** was prepared by the following sequence of reactions. Condensation of *p*-benzoquinonedibenzimide[12] with *o*-nitrobenzenethiol gave 2,5-dibenzamido-2′-nitrodiphenyl sulfide (86%), mp 230–234°. This sulfide was oxidized with hydrogen peroxide in glacial acetic acid to give 2,5-dibenzamido-2′-nitrodiphenyl sulfone (90%), mp 232–233°. The sulfone was hydrolyzed quantitatively with hot concentrated sulfuric acid (water bath) to give **6a**.

Reduction of the Derivatives of 2,5-Diamino-2′-nitrodiphenyl Sulfone (6). A.—A solution of **6a** (490 mg) was reduced with stannous chloride (5 g) by the method described above. The liberated base (340 mg) was recrystallized from aqueous methanol to give yellow cubes of **4a**, mp and mmp 167–168°.

B.—A solution of **6c** (1.3 g) in ethanol (100 ml) was hydrogenated (60 psi) in the presence of Raney nickel. The product was crystallized from ethanol to give white prisms of **4c**, mp and mmp 214–216°.

C.—A solution of **6d** (2.2 g) in dioxane (150 ml) and acetic acid (10 ml) was hydrogenated in the presence of Raney nickel for 15 hr. The greenish precipitate was recrystallized from aqueous dioxane to give white crystals of **4d**, mp 225–227°.

Oxidative Cyclization of 4d.—A solution of **4d** (1.1 g) and phenyliodoso acetate (1.8 g) in toluene (300 ml) was agitated overnight. The reaction mixture was warmed to dissolve the orange crystals and was then filtered to remove a red residue (85 mg). The filtrate was concentrated to a volume of 80 ml and was cooled to afford orange crystals, 854 mg, mp 294–300°. Recrystallizations from acetone gave **5d**, mp and mmp 305–307°. The reaction of **5d** with hydrazine solution in ethanol gave **5a**, mp and mmp 271–273°.

Compound **5d** (110 mg) was refluxed in a mixture of acetic acid (70 ml) and peracetic acid (7 ml) for 30 min. The solution was diluted with water to give a pale yellow precipitate (113 mg). This solid was recrystallized from acetic acid to give **7**, mp 307–309°. Compound **7** was also obtained when **4d** was oxidized with peracetic acid at room temperature. The reaction of **7** with hydrazine gave a poor yield of **5a**.

Reduction of 3.—The dinitro compound **3** (150 mg) was reduced with stannous chloride and concentrate hydrochloric acid to give a crude tetraamino compound, mp 149–153°. This crude product was treated with acetic anhydride in the presence of 1 *M* hydrochloric acid to give a precipitate (980 mg) which upon recrystallizations from isopropyl alcohol gave the analytically pure diacetyl derivative (**10**), mp 249–251°.

Registry No.—**2**, 30388-08-0; **3**, 30453-05-5; **4a**, 30388-09-1; **4b**, 30388-10-4; **4c**, 30388-11-5; **4d**, 30388-12-6; **5a**, 30388-13-7; **5d**, 30388-14-8; **6a**, 30388-15-9; **6c**, 30388-16-0; **6d**, 30388-17-1; **7**, 30388-18-2; **10**, 30388-19-3.

(19) T. Zincke and F. Farr, *Justus Liebigs Ann. Chem.*, **391**, 73 (1912).

Stabilized Sulfonium Ylides. II.[1] Ethyl Dimethylsulfuranylidene-2,4,6-trinitrophenylacetate

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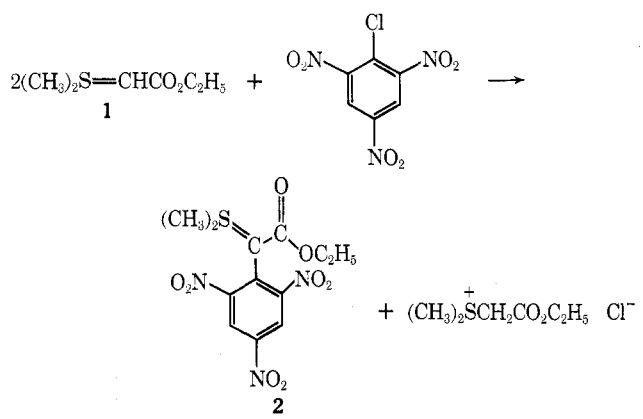
Although the nucleophilic properties and synthetic potential of carbonyl-stabilized sulfonium ylides have been the object of numerous studies in the past few years,[1,3] the behavior of these ylides as nucleophiles in nucleophilic aromatic substitution has not been explored. We report herein a case in which such substitution occurs with facility to produce a novel ylide with interesting properties.

When ethyl dimethylsulfuranylidenylacetate (**1**)[1,3i] and picryl chloride are mixed in a variety of solvents, either in the presence or absence of a tertiary amine, a



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(2) Department of Organic Chemistry, University of Lund, Sweden.

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