part of this substance was recrystallized from EtOAc; the pure orange crystals melted at 166° dec. *Anal.* ($C_6H_4Br_2N_2S$) C, H, N.

trans-**2-Bromo(4-nitrobenzenesulfonamido)cyclohexane (I).**—N,N-Dibromo-4-nitrobenzenesulfonamide (10 g) was added to a mixture of cyclohexene (30 ml) and CCl_4 (15 ml). A white precipitate appeared with slight evolution of heat. After the exothermic reaction subsided, the mixture was refluxed for 2.5 hr, and the precipitate was filtered with suction. Recrystallization (EtOH) gave colorless needles, mp 170–171°, yield 8.8 g (87.3%). *Anal.* ($C_{12}H_{15}BrN_2O_4S$) C, H, N.

trans-**2-Ethoxy-1-(4-nitrobenzenesulfonamido)cyclohexane (III).**—2-Bromo-1-(4-nitrobenzenesulfonamido)cyclohexane (I) (3 g) was added to a solution of Na (0.2 g) in absolute EtOH (30 ml). The mixture was refluxed on a steam bath for 2 hr. After the solution was cooled, 3.5% HCl (9.1 ml) was added and allowed to stand to yield 2.1 g (75%) of pale yellow needles, mp 140–141° (from MeOH). *Anal.* ($C_{14}H_{20}N_2O_5S$) C, H, N.

N-(4-Nitrobenzenesulfonyl)cyclohexenimine (II).—Dried Ag_2O (prepared from 3 g of $AgNO_3$), I (2 g), and Me_2CO (25 ml) were mixed and refluxed for 6 hr. The precipitate was filtered off and the filtrate was evaporated to dryness under reduced pressure. The residue was recrystallized (C_6H_6) giving pale yellow needles, mp 133–136°, yield 1.25 g (80.7%). This compound was also obtained by the treatment of I with AgOAc in C_6H_6. *Anal.* ($C_{12}H_{14}N_2O_4S$) C, H, N.

trans-**2-Acetoxy-1-(4-nitrobenzenesulfonamido)cyclohexane (IV).**—A mixture of II (0.5 g) and AcOH (3 ml) was refluxed for 3 hr. After cooling, H_2O (2 ml) was added; the white precipitate was recrystallized (EtOH) yielding yellow granules, 0.55 g (90%), mp 157–158°. *Anal.* ($C_{14}H_{18}N_2O_6S$) C, H, N.

trans-**2-Chloro-1-(4-nitrobenzenesulfonamido)cyclohexane (V).**—A mixture of II (0.564 g) and 13% HCl (4.2 ml) was refluxed for 3 hr. After cooling, the precipitate was collected and recrystallized (EtOH), mp 150–151°, yield 0.574 g (89%). *Anal.* ($C_{12}H_{15}ClN_2O_4S$) C, H, N.

Catalytic Reduction of Nitro Compounds I, III-V.—These compounds were reduced catalytically in EtOH (PtO_2) to the corresponding amino compounds (VI–IX, respectively) in good yields as follows: VI, mp 174–175° [*Anal.* ($C_{12}H_{17}BrN_2O_2S$) C, H, N]; VII, mp 105–106° [*Anal.* ($C_{14}H_{22}N_2O_3S$) C, H, N]; VIII, mp 157–158° [*Anal.* ($C_{14}H_{20}N_2O_4S$) C, H, N]; IX, mp 159–160° [*Anal.* ($C_{12}H_{17}ClN_2O_2S$) C, H, N]. VI was treated with Ac_2O to give *trans*-2-bromo-1-(4-acetamidobenzenesulfonamido)cyclohexane (X), mp 179–180° [*Anal.* ($C_{14}H_{19}BrN_2O_3S$) C, H, N].

Studies in Cinnoline Chemistry. I. The Synthesis of Substituted Phenyl Cinnolyl Sulfides

S. M. YARNAL AND V. V. BADIGER

Department of Chemistry, Karnatak University, Dharwar-3, India

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Cinnoline compounds have been recommended as drugs in the chemotherapy of trypanosomiasis,[1] as bactericides and antiparasites,[2] and in antitumor screening.[3] The antileukemic activity of various 4-substituted benzylthiocinnolines reported by Castle and his coworkers[4] aroused our interest in preparing a series of substituted phenyl cinnolyl sulfides and subjecting them for pharmacological screening. This paper describes the preparation of some new substituted-phenyl cinnolyl sulfides.

(1) J. R. Keneford, E. M. Lourie, J. S. Morley, J. C. E. Simpson, J. Williamson, and P. H. Wright, *J. Chem. Soc.*, 2595 (1952).

(2) E. P. Taylor, M. D. Potter, H. O. J. Collier, and W. C. Austin, British Patent 812,994 (May 6, 1959); *Chem. Abstr.*, **53**, 18971 (1959).

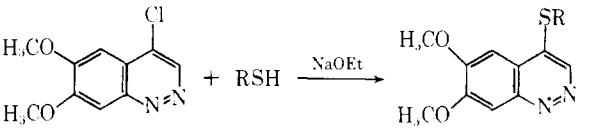
(3) R. N. Castle, H. Ward, N. White, and K. Adachi, *J. Org. Chem.*, **25**, 570 (1960).

(4) R. N. Castle, K. Adachi, and W. D. Guither, *J. Heterocyclic Chem.*, **2**, 459 (1965).

Experimental Section[5]

General Procedure.—The method is illustrated with the preparation of 2-chlorophenyl 4-(6,7-dimethoxycinnolyl) sulfide. To a dry solution of NaOEt from Na (0.02 g-atom) in absolute EtOH (20 ml) under N_2 was added with shaking *o*-chlorothiophenol (0.02 mole) followed by addition of 0.02 mole of 4-chloro-6,7-dimethoxycinnoline.[6] The reaction mixture was refluxed for 2 hr under N_2, diluted with sufficient H_2O, and made alkaline to dissolve the unreacted thiophenol. The solid material was filtered and recrystallized from dilute EtOH: mp 164 (5°), yield 1.5 g. Compounds prepared in this way are listed in Table I.

TABLE I



No.	R	Yield,[a] %	Mp, °C	Formula[b]
1	C_6H_5	72	165	$C_{16}H_{14}N_2O_2S$
2	*p*-$CH_3C_6H_4$	94	181–182	$C_{17}H_{16}N_2O_2S$
3	*o*-ClC_6H_4	75	152	$C_{16}H_{13}ClN_2O_2S$
4	*m*-ClC_6H_4	34	176–177	$C_{16}H_{13}ClN_2O_2S$
5	*p*-ClC_6H_4	47	199	$C_{16}H_{13}ClN_2O_2S$
6	2,5-$Cl_2C_6H_3$	67	200–201	$C_{16}H_{12}Cl_2N_2O_2S$
7	3,5-$Cl_2C_6H_3$	58	177–178	$C_{16}H_{12}Cl_2N_2O_2S$
8	3,4-$Cl_2C_6H_3$	68	192	$C_{16}H_{12}Cl_2N_2O_2S$[c]

[a] All compounds were recrystallized from EtOH–H_2O. [b] All compounds were analyzed satisfactorily for C, H, N. [c] This compound was analyzed satisfactorily for C, H.

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(5) Melting points were taken in capillary tubes and are uncorrected.

(6) R. N. Castle and F. H. Kruse, *J. Org. Chem.*, **17**, 1571 (1952).

N,N,N′,N′-Tetraalkylhomopiperazinium Salts[1]

WILLIAM F. HART AND KENNETH E. JONES

Department of Chemistry, Lafayette College, Easton, Pennsylvania 18042

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The availability of homopiperazine (1,4-diazacycloheptane) by a novel and simple synthesis[2] has made it possible to prepare a series of symmetrical N,N′-dialkylhomopiperazines and their quaternary ammonium salts. The bis-quaternary dimethosulfates were prepared for the purpose of determining their bactericidal properties in comparison with homologous compounds derived from N,N′-dialkylpiperazines and with N-alkyl-N-methylpyrrolidinium methosulfates and N-alkyl-N-methylmorpholinium and -thiamorpholinium methosulfates previously described.[3]

Experimental Section[4]

Symmetrical N,N′-dialkylhomopiperazines (Table I) were prepared by refluxing 5 g (0.05 mole) of homopiperazine with

(1) Abstracted in part from the thesis of K. E. Jones presented to Lafayette College in partial fulfillment of the requirements for the degree of B.S. in Chemistry, June 1964.

(2) F. Poppelsdorf and R. C. Myerly, *J. Org. Chem.*, **26**, 131 (1961).

(3) (a) D. R. Smith, J. W. Curry, and R. L. Eiffert, *J. Am. Chem. Soc.*, **72**, 2969 (1950); (b) W. F. Hart and M. E. McGreal, *J. Org. Chem.*, **22**, 81 (1957); (c) *ibid.*, **22**, 87 (1957), and references cited therein.

(4) Melting points were taken in capillary tubes and are corrected. Elemental analyses were determined by Drs. Weiler and Strauss, Oxford, England. Where analyses are indicated only by symbols of the elements, analytical results obtained for those elements are within ±0.4% of the theoretical value.