

all negative. The Keller reaction, concd. sulfuric acid containing a trace of ferric ion, was positive.

Anal. Calcd. for $C_{33}H_{50}N_4S_2$: C, 72.79; H, 7.99; N, 8.94; S, 10.23. Found: C, 72.50; H, 8.04; N, 9.06; S, 10.33.

Ultraviolet spectrum: λ_{max} (log ϵ) 300 (3.56); 212 (4.30).

Infrared spectrum (potassium bromide): 2.95–2.98 (broad); 3.43; 3.58; 6.05vw; 6.20vw; 6.44s; 6.86vs; 7.25m; 7.39s; 7.52w; 7.86m; 8.10m; 8.28m; 8.39s; 8.56w; 8.74m; 8.86m; 9.08w; 9.37w; 9.74m; 9.88m; 10.0vw; 10.11vw; 10.36m; 10.69w; 11.51m μ .

On reductive hydrolysis of the disulfide (10 mg.) with zinc in acetic acid the ether solution of the crude reaction product showed (in chloroform) a band at 5.81 μ of medium intensity, and 6.20vs, both bands typical of oxindole derivatives. However, on purification of the material *via* the picrate only a small amount of quebrachamine picrate, m.p. 193°, identified by mixed melting point and infrared spectrum, was obtained. The same result was given by the reduction of the disulfide with Raney nickel.

Quebrachamine "tribromide." *N*-Bromosuccinimide (0.222 g.) was added slowly with mechanical stirring to 0.141 g. of quebrachamine in 3 ml. of glacial acetic acid and 2 ml. of water. Stirring was continued for 1 hr. at room temperature and then 4*N* sodium hydroxide was added in the cold until the solution was at pH 6. Extraction with dichloromethane and *n*-propyl alcohol yielded a yellow oil which was crystallized from chloroform and benzene to yield 0.08 g. of cotton-like needles, m.p. 287–289°. The analytical sample was prepared by a recrystallization from the same solvents. It displayed m.p. 290°, ultraviolet spectrum λ_{max} 231 (ϵ 44,000), 285 (ϵ 7,440), 293 (ϵ 7,470) and had no carbonyl absorption in the infrared.

Anal. Calcd. for $C_{19}H_{23}N_2Br_3$: C, 43.96; H, 4.47; Br, 46.18. Found: C, 43.99; H, 4.59; Br, 45.99. The formula $C_{19}H_{25}N_2Br_3$ (C, 43.79; H, 4.84; Br, 46.00) is not excluded.

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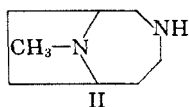
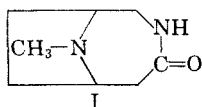
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Synthesis of 9-Methyl-3,9-diazabicyclo[4.2.1]-nonane

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This note reports the preparation of the title compound, II, by treatment of tropinone with hydrazoic acid to give the bicyclic lactam I which was reduced with lithium aluminum hydride. The overall yield of II was 61%.



This scheme provides access to a bicyclic homopiperazine system of potential value as an intermediate for compounds of pharmacological interest.

EXPERIMENTAL

9-Methyl-3,9-diazabicyclo[4.2.1]nonan-4-one (I). A solution of 11.1 g. (0.08 mole) of tropinone in 100 ml. of chloroform cooled to -5° in an ice-salt bath was treated dropwise with stirring with 25 ml. of concentrated sulfuric acid, keeping the temperature below 15° . After cooling to 5° the stirred reaction mixture was treated with 10.4 g. (0.16 mole) of sodium azide in approximately 0.5–1 g. portions at such a rate that the temperature did not exceed 35° . Addition of the azide required about 2 hr. after which the reaction mixture was stirred at 50° for another 2 hr. It was then poured into a 600 ml. beaker one third filled with ice. Solid potassium carbonate was added portionwise until the mixture was strongly alkaline. This was followed by 50 ml. of a 60% potassium hydroxide solution; the inorganic salts were removed by filtration and washed well with chloroform. The alkaline filtrate was extracted with three portions of chloroform and the combined chloroform washings and extracts were dried over anhydrous sodium sulfate. Filtration of the drying agent followed by removal of the chloroform by distillation gave 11.1 g. (90%) of crude I, m.p. 79–83°. For analysis, a sample was converted to the hydrochloride, m.p. 258–259° dec. (from ethanol).

Anal. Calcd. for $C_8H_{15}ClN_2O$: C, 50.39; H, 7.93; N, 14.69. Found: C, 50.42; H, 7.96; N, 14.59.

9-Methyl-3,9-diazabicyclo[4.2.1]nonane (II). To a solution of 11.0 g. (0.071 mole) of I in 400 ml. of dry ether was added dropwise with stirring under an atmosphere of dry nitrogen, a solution of 6.8 g. (0.18 mole) of lithium aluminum hydride in 200 ml. of dry ether. Addition was complete in 0.5 hr., and the mixture was stirred and refluxed for 46 hr.

Water (25 ml.) was added dropwise to the cooled reaction mixture which was then filtered by suction. The filter cake was washed well with ether and the combined filtrate and washings were dried over anhydrous sodium sulfate. Filtration and removal of the ether by distillation followed by vacuum distillation of the residual oil gave 6.8 g. (68%) of II, b.p. 111–113° (38 mm.), n_D^{25} 1.4992.

Anal. Calcd. for $C_8H_{16}N_2$: C, 68.52; H, 11.50; N, 19.98. Found: C, 68.71; H, 11.91; N, 20.26.

II. Dihydrochloride, m.p. 290–291° dec. (from dry ethanol).

Anal. Calcd. for $C_8H_{16}Cl_2N_2$: C, 45.08; H, 8.51. Found: C, 45.46; H, 8.61.

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Preparation of *m*- and *p*-Diethynylbenzenes

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We wished to prepare reasonably large quantities of *m*- and *p*-diethynylbenzenes. Deluchat¹

(1) R. Deluchat, *Ann. chim.*, 1 [11] 181–255 (1934).