

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.

Acknowledgment. We are greatly indebted to Drs. K. Freter and A. A. Patchett for experimental assistance, to Dr. H. Conroy for helpful discussions and to Dr. G. F. Smith for an advance copy of his manuscript prior to publication.

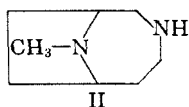
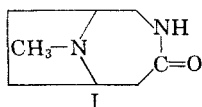
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Synthesis of 9-Methyl-3,9-diazabicyclo[4.2.1]-nonane

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Received September 29, 1959

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.

Acknowledgment. The authors are indebted to Mr. E. F. Shelberg and his associates for the microanalyses.

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

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Received September 30, 1959

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

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

had prepared these compounds by a laborious seven step synthesis starting from the corresponding xylene isomer. This route was obviously not satisfactory for relatively large scale preparation of these materials.

When the commercially available divinylbenzene mixture² (40% *m*- and *p*-divinylbenzenes) is brominated in chloroform solution, 1,4-bis(1,2-dibromoethyl)benzene separates on cooling. Recrystallization from chloroform yields the pure material. The bromination residue now contains 1,3-bis(1,2-dibromoethyl)benzene along with considerable quantities of the dibromodiethylbenzenes from the ethylstyrenes in the starting material. A molecular distillation readily separates the dibromodiethylbenzenes from the tetrabromodiethylbenzene. The latter fraction on crystallization from ethanol yields pure 1,3-bis(1,2-dibromoethyl)benzene. Treatment with four moles of potassium *t*-butoxide in *t*-butanol readily converts the tetrabromodiethylbenzenes to the respective diethynylbenzenes.

EXPERIMENTAL

Bromination of mixed divinylbenzenes. Bromine (1300 g., 8.13 moles) was added over 2 hr. with stirring to a cooled solution of 750 g. mixed divinylbenzene (40% = 2.3 moles *m*- and *p*-divinylbenzene) in 1200 ml. of chloroform. The reaction mixture was then cooled to 5° and a voluminous precipitate settled out which was separated by filtration. Recrystallization from chloroform yielded 264 g. (0.59 mole) of 1,4-bis(1,2-dibromoethyl)benzene, m.p. 155–157° (lit.¹ m.p. 157°). The two filtrates were combined and the chloroform removed on a rotating evaporator at 100° (3 mm.). The residue was then fractionated in a molecular still. Distillation at 50° (40–70 μ) and then at 80° (20–50 μ) separated most of the dibromodiethylbenzenes. The residue which was a viscous sirup was distilled at 150° (12–30 μ). The distillate crystallized when triturated with cold alcohol and after recrystallization from alcohol yielded 420 g. (0.93 mole, combined yield of 66%), 1,3-bis(1,2-dibromoethyl)benzene, m.p. 65–66.5° (lit.¹ m.p. 64°).

***p*-Diethynylbenzene.** To a solution of 18 g. (0.46 mole) of potassium in 1 l. of *t*-butanol at the temperature of reflux was added 50 g. (0.11 mole) of 1,4-bis(1,2-dibromoethyl)benzene. After 1 hr. the reaction mixture was made up to 4 l. with ice water and the pale yellow solid was removed by filtration. There was isolated 9.8 g. (0.078 mole, 71% yield) of *p*-diethynylbenzene, m.p. 95° (lit.¹ m.p. 95°). Sublimation at 90–100° (2 mm.) gave a colorless solid m.p. 96.5°.

***m*-Diethynylbenzene** was prepared in an identical fashion and in comparable yield from 1,3-bis(1,2-dibromoethyl)benzene. After flooding with water the product was isolated by ether extraction and distillation to yield *m*-diethynylbenzene, b.p. 78° (14 mm.), n_D^{20} 1.5825 (lit.¹ b.p. 78° (15 mm.) n_D^{18} 1.5841).

Acknowledgment. The distillations were performed by Mr. E. M. Hadsell. It is a pleasure to acknowledge the very capable assistance of Mr. R. J. Flatley.

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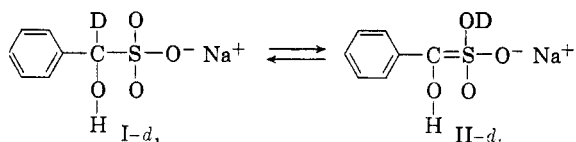
(2) Purchased from Monomer-Polymer Laboratories, 5000 Langdon Street, P.O. Box 9522, Philadelphia 24, Pa.

Absence of Exchange by the "Aldehydic" Hydrogen of Benzaldehyde Sodium Bisulfite

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Received October 19, 1959

In 1939 Thompson and Cromwell reported that in contrast to the lack of hydrogen-deuterium exchange by aldehydes, benzaldehyde-*d*₁ sodium bisulfite (I-*d*₁) exchanged up to 76% with conductivity water in a period of seventeen days.¹ They suggested that this could be evidence for the enolization of the bisulfite complex. Such an enol form (II-*d*₁) would be of particular interest since it postulates an expanded valence shell of ten electrons for the sulfur atom in the complex.



We desired to prepare some deuterated benzaldehydes by utilizing the reverse of this reported exchange reaction. We first attempted to prepare benzaldehyde-*d*₁ by placing benzaldehyde sodium bisulfite (I) in excess deuterium oxide for a long period of time, as indicated in experiment 1, Table I. The infrared spectrum of the aldehyde showed that no exchange had occurred.² Similar experiments (2, 4, and 5 through 9) were made using different methods of separating the products, and of determining the extent of exchange by infrared analysis. These experiments were conducted under various conditions such as exposure to near ultraviolet light or in the presence of added substances which might somehow have acted as catalysts in the original work. Experiment 3 is essentially a duplication of one experiment of the reported exchange reaction, using benzaldehyde prepared from lithium aluminum deuteride.² In every experiment no hydrogen-deuterium exchange was found on the "carbonyl" carbon of I or I-*d*₁. Thus, there is no evidence for the existence of an enol form, such as II-*d*₁.

The attempted exchange experiments are summarized in Table I. The infrared spectra of I and I-*d*₁ are shown in Fig. 1. The deuterated complex is readily distinguished from I by the absence of bands at 1411 and 845 cm^{-1} and the presence of bands at 1347, 969, 945, and 766 cm^{-1} .

(1) A. F. Thompson, Jr., and N. H. Cromwell, *J. Am. Chem. Soc.*, **61**, 1374 (1939).

(2) K. B. Wiberg, *J. Am. Chem. Soc.*, **76**, 5371 (1954).

(3) Deutero-benzaldehyde is easily distinguished from benzaldehyde by the large shift in the C—H stretching frequency (*cf.* ref. 2), and also shows the absence of bands at approximately 1387, 826, and 714 cm^{-1} and the presence of bands at approximately 1222, 791, and 733 cm^{-1} .