dithiol in 100 cc. of acetic acid, followed by 4 cc. of boron fluoride etherate. Crystals of the high-melting bis-product started separating in about one-half hour; after standing overnight the crystallized bis-product was collected (0.55 g.) and the material in the mother liquor recovered by ether extraction. A little starting material was removed by extraction of a petroleum ether solution of the product with Claisen's alkali. After concentration of the petroleum ether solution, the monoketal separated in crystalline condition, m.p. 156° (0.3 g.). The substance is sparingly soluble in methanol and readily soluble in hot hexane. It crystallized slowly from hexane in massive clusters of short needles, m.p. 158.5–159.5°, α_D +81.2° Chf (*c* 2.03), λ^{EtOH} 244 mμ (7,170), λ^{Chf} 5.93, 6.19 μ.

Anal. Calcd. for $C_{29}H_{46}OS_2$ (474.66): C, 73.38; H, 9.77. Found: C, 73.48; H, 9.73.

Desulfurization of this product with active Raney nickel was accomplished by refluxing in dioxane for 7 hr.[15] or in absolute ethanol for 9 hr.[11] In the first case, 1.5 g. of derivative gave 0.65 g. of white solid m.p. 88–93°, and five recrystallizations gave glistening white leaflets of **cholestane-6-one**, m.p. 97–99°, α_D +2.5° Chf (*c* 1.83), λ^{Chf} 5.87 μ, no ultraviolet absorption at 243 mμ; oxime, m.p. 186–191° dec., no depression on admixture with the above sample. Desulfurization[11] in boiling dioxane (7 hr.) with Raney nickel deactivated by refluxing it with acetone[9] and chromatography of the product gave Δ^4-cholestene-6-one as needles from ethanol, m.p. 108–109°, α_D +31.6° Chf (*c* 1.43), λ^{Chf} 6.00, 6.20 mμ, λ^{EtOH} 242 mμ (3,846); this did not depress the m.p. of an authentic sample of comparable constants.

Cholestane-3-one Ethylenethioketal.—A solution of 600 mg. of cholestanone and 1 cc. of ethanedithiol in 15 cc. of hot acetic acid was treated with 1 cc. of boron fluoride etherate and let stand to crystallize. Excellent needles separated and were collected and washed with methanol; 662 mg. (92%), m.p. 142–144°. Recrystallization from acetone or from dioxane–ethanol gave long flat needles, m.p. 146.5–147.5°, α_D +32.0° Chf (*c* 2.09).

Anal. Calcd. for $C_{29}H_{50}S_2$ (462.69): C, 75.28; H, 10.89. Found: C, 75.11; H, 10.88.

Cholestane-3-one Ethylenehemithioketal (*cf.* ref. 6).—A solution of 130 mg. of cholestanone in 6 cc. of acetic acid was treated at 25° with 0.2 cc. of β-mercaptoethanol and 0.5 cc. of boron fluoride etherate and left undisturbed. Crystallization soon commenced, and when it seemed complete, methanol was added and the product collected; 124 mg., m.p. about 130°. The substance is only moderately soluble in ethanol and separated in glistening slender needles, m.p. 133–134° (104 mg.); recrystallized, m.p. 133–134°, α_D +24.8° Chf (*c* 0.681).

Anal. Calcd. for $C_{29}H_{50}OS$ (446.69): C, 77.97; H, 11.28. Found: C, 78.34; H, 11.40.

Δ^5-Cholestene-3-one Ethylenehemithioketal.—On addition of 0.4 cc. of β-mercaptoethanol and 1 cc. of boron fluoride etherate to a suspension of 368 mg. of Δ^5-cholestene-3-one in 10 cc. of acetic acid at 25°, the reaction product started to separate before the ketone had all dissolved. The mixture was stirred well, diluted with methanol, and 100 mg. of product collected (m.p. about 130°). This crystallized nicely from ethanol in cottony clusters of fine needles (76 mg.), m.p. 136–137° (unchanged on recrystallization, α_D −19.6° Chf (*c* 0.847).

Anal. Calcd. for $C_{29}H_{48}OS$ (444.67): C, 78.32; H, 10.88. Found: C, 78.57; H, 11.11.

The low yield is undoubtedly because of isomerization to the conjugated ketone before condensation is complete. Thus attempted condensation of 307 mg. of Δ^5-cholestene-3-one with ethylene glycol under comparable conditions afforded 114 mg. of Δ^4-cholestene-3-one, m.p. 80–81°, mixed m.p. 81–82°.

Derivatives of Dehydroepiandrosterone. (a) Ethylenethioketal Acetate.—A solution of 300 mg. of dehydroepiandrosterone acetate, 0.3 cc. of ethanedithiol and 0.3 cc. of boron fluoride etherate in acetic acid at 25° soon deposited crystals. A little water was added and the crystals were collected and washed with methanol; 343 mg. m.p. 190°. The derivative crystallized from 95% ethanol in large, thin plates, m.p. 191–192°, α_D −86.4° Chf (*c* 2.14).

Anal. Calcd. for $C_{23}H_{34}O_2S_2$ (406.50): C, 67.95; H, 8.43. Found: C, 68.03; H, 8.46.

(b) **Ethylenehemithioketal Acetate.**—Similar condensation of 300 mg. of the acetate with β-mercaptoethanol gave 310 mg. of product, m.p. 166–170°. Crystallized from 95% ethanol, the substance formed long blades, m.p. 183–184° (unchanged on recrystallization), α_D −99.5° Chf (*c* 2.08).

Anal. Calcd. for $C_{23}H_{34}O_3S$ (390.50): C, 70.74; H, 8.78. Found: C, 70.72; H, 8.82.

(c) **Ethyleneketal.**[16]—A solution of 1.5 g. of dehydroepiandrosterone and 1.5 g. of ethylene glycol in 80 cc. of benzene was distilled in a water separator until dry, 100 mg. of *p*-toluenesulfonic acid was added, and the solution was refluxed overnight in the water take-off apparatus. Ether extraction and crystallization from aqueous methanol (with addition of a drop of pyridine) gave 1.0 g. (59%) of product, m.p. 161–165°.

Anal. Calcd. for $C_{21}H_{32}O_3$ (332.47): C, 75.86; H, 9.71. Found: C, 75.71; H, 9.80.

The **acetate** crystallized from aqueous methanol in beautiful plates, m.p. 140–142°, α_D −83.5° Chf (*c* 2.06).

Anal. Calcd. for $C_{23}H_{34}O_4$ (374.50): C, 73.76; H, 9.15. Found: C, 73.53; H, 9.31.

(d) **3β-Acetoxy-Δ^5-androstene-7-one 17-Ethyleneketal**[16] was obtained by chromic acid oxidation of the acetate (c) at 55–60° (5 hr.). The keto derivative, crystallized from aqueous methanol, melted at 175–177°, $\lambda^{\mathrm{CCl_4}}$ 5.95 μ.

Anal. Calcd. for $C_{23}H_{32}O_3$ (388.49): C, 70.95; H, 8.51. Found: C, 71.10; H, 8.30.

Δ^4-Cholestene-3-one Ethylenethioketal.—A solution of 1 g. of Δ^4-cholestene-3-one in 5 cc. of acetic acid, treated at 25° with 0.5 cc. of ethanedithiol and 0.5 cc. of boron fluoride etherate, warmed up and in 1–2 min. set to a stiff paste. After 15 min. the product was collected and washed with methanol: 1.15 g. (96%), m.p. 117–118°. Crystallization from acetone–methanol gave slender, flat needles, m.p. 117.5–118.5°; recrystallized: 118.5–119.5°, α_D + 111.8° Chf (*c* 2.03); Hauptmann,[1] m.p. 106–107°, α_D + 119° Chf.

Anal. Calcd. for $C_{29}H_{48}S_2$ (460.67): C, 75.60: H, 10.50. Found: C, 75.38; H, 10.58.

Benzil Monoethylenethioketal.—A solution of 1 g. of benzil in 4 cc. of acetic acid at 25° was treated with 1 cc. each of ethanedithiol and boron fluoride etherate and let stand undisturbed. The yellow color was slowly discharged after about one day, and on the second day the product separated in large prismatic needles; 1.0 g., m.p. 93–94°. Recrystallization from ethanol (best by seeding) raised the m.p. to 95–96°, λ^{Chf} 5.97, 6.25, 6.31 μ.

Anal. Calcd. for $C_{16}H_{14}OS_2$ (286.27): C, 67.12; H, 4.93. Found: C, 66.85; H, 4.87.

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(15) Experiment by Freeland E. Romans.

(16) Experiment by Josef E. Herz.

CAMBRIDGE, MASS.

9-Methyl-3,9-diazatricyclo[3.3.1.2^{3,9}]undecane

BY HENRY M. FALES AND RODERICK A. BARNES

RECEIVED DECEMBER 28, 1953

In a recent description of the synthesis of the 3,9-diazabicyclo[3.3.1]nonane ring system[1] the possibility of linking the two nitrogen atoms with an ethylene bridge was mentioned. With the realization of this possibility we have now prepared the first example of a substance in which four six-membered rings are linked in this kind of tricyclic system.

Ethylene bromide reacted smoothly with 9-methyl-3,9-diazabicyclo[3.3.1]nonane (I) in toluene at 40°. Both the crystalline bromide and picrate salts of the resulting quaternary ammonium base II were obtained.

The only substances, other than II, which could logically have the observed analysis are the 3- or 9-vinyl derivatives of I or a dimeric product re-

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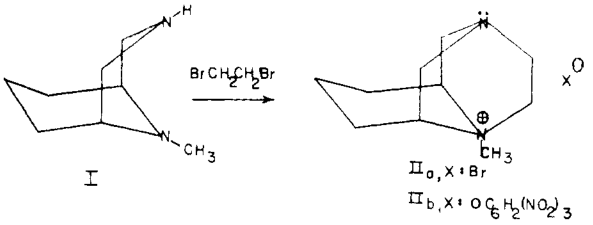
(1) R. A. Barnes and H. M. Fales, THIS JOURNAL, **75**, 975 (1953).



I

IIa, X = Br

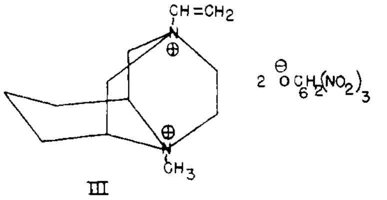
IIb, X = OC$_6$H$_2$(NO$_2$)$_3$

sulting from establishment of ethylene bridges between the nitrogen atoms of two molecules of I.

The 9-vinyl structure is eliminated because the infrared curve for IIb shows no absorption at 2.9–3.2 μ (N–H band). The 3-vinyl structure is also eliminated since this would be a di-tertiary amine containing no quaternary nitrogen atom.

The observation by Mann and Mukherjee[2] that only traces of a dimeric substance were formed in the reaction of N,N′-dimethylpiperazine with ethylene bromide strongly suggests that II is monomeric. As these authors point out, the dimeric compound demands effectively planar piperazine rings in order to preserve the normal intervalency angle of tri- or tetracovalent nitrogen (*ca.* 110°). Even less dimer might be expected from I since favored configurations of this bicyclic system require a puckered piperazine ring.

When the reaction was run with an excess of ethylene bromide at 130° the sole product isolated upon addition of lithium picrate was a neutral quaternary ammonium picrate whose analysis agreed with the values calculated for compound III.



III

This substance could have resulted from the reaction of IIa with additional ethylene bromide followed by elimination of hydrogen bromide. Compound III exhibited two peaks (6.12, 6.20 μ) in the infrared region assigned to double bonds while compound IIb showed only one peak at 6.08 μ.

Experimental[3]

9-Methyl-3,9-diazabicyclo[3.3.1]nonane (I).—This compound, isolated previously as a dihydrochloride, was obtained as the free base by adding strong alkali to a concentrated aqueous solution of the hydrochloride followed by rapid extraction with ether. Evaporation of the dried solvent left a volatile semi-crystalline mass having a typical amine odor. The compound rapidly absorbed carbon dioxide and water from the air forming a solid carbonate, m.p. 69–70° dec.

The free amine was repeatedly sublimed at 70° (15 mm.) finally forming short prisms, m.p. 62–65° (sealed, evacuated capillary). Recrystallization was impossible since the compound was very soluble in ice-water, alcohols and even cold petroleum ether.

Anal. Calcd. for $C_8H_{16}N_2$: N, 19.98. Found: N, 19.24 (by $HClO_4$ titration in glacial acetic acid).

The dihydriodide after recrystallization from water did not decompose up to 280°.

Anal. Calcd. for $C_8H_{18}N_2I_2$: C, 24.26; H, 4.58. Found: C, 24.18; H, 4.62.

The presence of a secondary amine was demonstrated by the preparation of an N-picryl picrate. A small sample of the free amine was treated with an excess of picryl chloride in ethanol. After the solution had been allowed to stand overnight, a concentrated solution of lithium picrate was added and the N-picryl picrate precipitated. After three recrystallizations from dimethylformamide–ethanol mixtures the product melted at 263–266° dec.

Anal. Calcd. for $C_{20}N_8O_{13}$: C, 41.38; H, 3.47. Found: C, 41.84; H, 3.52.

9-Methyl-3,9-diazatricyclo[3.3.1.2^{3,9}]undecane Picrate (IIb).—The carbonate of I (0.53 g.) was heated in 10 ml. of toluene to drive off water and carbon dioxide. Ethylene bromide (0.75 g.) was added to the cooled solution which was then allowed to stand at 40° for several days. After removing the toluene and excess ethylene bromide on the aspirator a basic solution of lithium picrate was added and the precipitated salt collected and washed with ether. The dried product (0.44 g., *ca.* 64%) was recrystallized from either formamide–isobutyl alcohol or dimethylformamide–ethanol mixtures and formed long brown needles. Successive recrystallizations caused the picrate to become bright yellow, m.p. 275–280° (dec. without evolving gas).

Anal. Calcd. for $C_{16}H_{21}N_5O_7$: C, 48.60; H, 5.35. Found: C, 48.42, 48.56; H, 5.62, 5.40.

The corresponding bromide (IIa) was obtained through quaternization as above followed by evaporation of solvents and addition of 98% ethanol. This precipitated the dihydrobromide salt of unchanged starting material. Evaporation of the mother liquors from this precipitate left a crystalline product which was crystallized from alcohol–ethyl acetate or moist isobutyl alcohol. The product apparently retained water of crystallization even when dried at 100° (0.005 mm.); m.p. 243–247°.

Anal. Calcd. for $C_{10}H_{19}N_2Br \cdot H_2O$: C, 45.29; H, 7.98; N, 10.57. Found: C, 45.65; H, 7.96; N, 10.47.

A sample of the bromide was treated with aqueous lithium picrate and the resulting precipitate recrystallized from dimethylformamide–ethanol. The resulting light-yellow needles decomposed at 275–280°. For substances of this type the mixture melting point technique is unreliable, therefore X-ray diffraction photographs were taken both of the picrate from the above bromide and that obtained directly. Their powder diagrams were identical.

Both of the above picrates formed salts with additional picric acid. After recrystallization from dimethylformamide–ethanol the salts both decomposed at 225–230° and evolved picric acid.

Compound III, suspected to have the structure shown, was obtained by suspending a sample of the carbonate (1.44 g.) of I in a large excess of ethylene bromide (4.0 g.) and refluxing the solution for 20 minutes. Evaporation of the ethylene bromide and addition of basic lithium picrate precipitated a light-yellow solid (0.925 g.). After several recrystallizations from dimethylformamide–isobutyl alcohol mixtures the silky yellow needles decomposed at 272–280°. This compound did not combine with additional picric acid.

Anal. Calcd. for $C_{24}H_{26}N_8O_{14}$: C, 44.31; H, 4.03; N, 17.23. Found: C, 44.70; H, 4.31; N, 17.29.

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[2] F. G. Mann and Deb. P. Mukherjee, *J. Chem. Soc.*, 2298 (1949).

[3] Microanalyses by W. Manser, Zurich, Switzerland, and J. F. Alicino, Metuchen, N. J. All melting points were observed on a Köfler hot-stage.

Triazines. VII. The Reaction of Cyanuric Chloride with Lithium Aluminum Hydride[1]

BY CHRISTOPH GRUNDMANN AND ELFRIEDE BEYER

RECEIVED DECEMBER 2, 1953

Recently Burger and Hornbaker[2] described the reduction of cyanuric chloride with lithium aluminum hydride which leads to formation of 2-dimeth-

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[1] Paper VI, C. Grundmann and A. Kreutzberger, THIS JOURNAL, **76**, 632 (1954).

[2] A. Burger and E. D. Hornbaker, *ibid.*, **75**, 4579 (1953).