appear in Table I. In all cases, only expected components appeared in vpc traces. Olefin composition was varied in duplicate experiments.

Control Experiments.—The thermal conductivity detector was calibrated with purified adduct mixtures. With exception of VIIIc (see above) the observed correction factors were quite similar to expectations.[38]

The stability of products to reaction conditions was demonstrated for every competitive pair reported in the table. An example follows. Crude product mixture (VIIIc, 39.0 mg) and crude product mixture (VIIIe, 36.0 mg) were dissolved in 0.5 ml of *t*-butylethylene. Vpc gave VIIIc/VIIIe as 0.84. Another 9.5 ml of *t*-butylethylene was added, followed by DCPD to *ca.* 0.034 *M*. Irradiation and work-up afforded a residue which was submitted to vpc. The trace showed that VIIId had formed in yield comparable with the adducts originally present. VIIIc/VIIIe was 0.86. Results of other control experiments appear above.

Acknowledgments.—Financial support by the National Science Foundation, GP-4857, and (in part) by the Research Council of Rutgers, the State University, New Brunswick, N. J., was sincerely appreciated.

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[38] N. Brenner, J. E. Callen, M. D. Weiss, Ed., "Gas Chromatography," Academic Press Inc., New York, N. Y., 1962, pp 231-327.

Dodecahydro-1,4,7,9b-tetraazaphenalene, a Condensate of Acrolein and Ammonia

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Dodecahydro-1,4,7,9b-tetraazaphenalene (I), a new substance, has been obtained in high yield by the condensation of acrolein and ammonia at 150°. Its structure was established by spectral studies and by the nature of the products obtained from several of its chemical reactions. Oxidation of I with mercuric acetate introduced a carbon–nitrogen double bond in a position allylic to the central nitrogen. Heating I to 250° with a palladium catalyst gave 4-amino-2-ethylpyrimidine as a degradation product. Oxidation with potassium permanganate afforded 1,5,9-triazacyclododecane-4,8,12-trione. A number of other reactions of I have been investigated. Condensations of methacrolein and crotonaldehyde with ammonia yielded substances which appear to be homologs of the acrolein–ammonia condensate.

The reactions of acrolein with ammonia have been well explored.[1] Spectroscopic studies have indicated that mixtures of the two compounds do not react at temperatures below −130°. In the range −130 to about −60° the carbonyl function disappeared and it was evident from spectral data and elemental analyses of precipitated products that the simple carbonyl-addition compounds, $CH_2{=}CHCH(OH)NH_2$ and $CH_2{=}CHCH(OH)NHCH(OH)CH{=}CH_2$, were formed. These products on being warmed to 0° evolved acrolein and ammonia and formed condensates containing formyl, amino, and imino groups.

At temperatures above 0°, acrolein and ammonia combine by additions both to the carbonyl and the vinyl group, and the products characteristically have been polymeric condensates and mixtures of simple nitrogen base compounds. Reactions in methanol at 50° have given solid nitrogen-rich polymers, and condensations in the presence of hydrogen and a nickel catalyst, in aqueous methanol at 125°, have yielded 1,3-diaminopropane, *n*-propylamine, di-*n*-propylamine, and higher molecular weight condensates. Vapor phase reactions at 350° over acidic catalysts, with steam as diluent, have given mixtures of pyridine, β-picoline, and higher boiling nitrogen bases.

It has now been found[2] that under certain conditions 3 moles of acrolein and 4 of ammonia condense in the liquid phase to form a new substance, $C_9H_{18}N_4$, identified as dodecahydro-1,4,7,9b-tetraazaphenalene (I). The reaction proceeds readily in methanol at temperatures of 140–150°, and the yield is at least 85% under optimum conditions. The isolated product is a white, hydroscopic crystalline solid, melting at 118–120°.

Methacrolein and crotonaldehyde combine with ammonia under similar conditions, affording condensates of composition $C_{12}H_{24}N_4$ in 49 and 94% distilled yields, respectively. The structures of these two substances have not been established by chemical means, but on the basis of composition, molecular weight, and spectral data they are believed to be homologs of the acrolein–ammonia condensate. Accordingly, the methacrolein derivative is tentatively assigned structure II, 3,6,9-trimethyldodecahydro-1,4,7,9b-tetraazaphenalene, and the crotonaldehyde derivative, structure III, 2,5,8-trimethyldodecahydro-1,4,7,9b-tetraazaphenalene.

Structure III is also the structure that Delépine,[3] on the basis of skilled and imaginative studies, proposed for the "tricrotonylenamine" (tricrotonylidene tetramine), $C_{12}H_{24}N_4$, that Wurtz[4] obtained in 1879 on heating either aldol or crotonaldehyde with ammonia in sealed containers. The source and composition of the Wurtz product suggest that it was, indeed, the same substance as our crotonaldehyde–ammonia condensate, but this has not been demonstrated in any manner. Further, similarities in chemical properties and results of oxidative degradation indicate that the Wurtz compound, as described by Delépine,[3] and our acrolein–ammonia condensate, I, are homologous substances.

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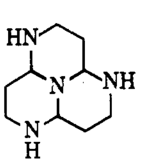
[1] See H. D. Finch, "Acrolein," C. W. Smith, Ed., John Wiley and Sons, Inc., New York, N. Y., 1962, Chapter 6, pp 96–109, for a review of the reactions of acrolein with ammonia and other nitrogen bases.

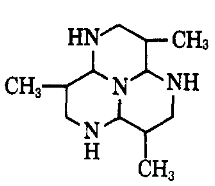
[2] J. L. Van Winkle, U. S. Patent 3,112,315 (Nov 26, 1963).

[3] (a) M. Delépine, *Compt. Rend.*, **144**, 853 (1907); (b) *ibid.*, **216**, 649; (c) *ibid.*, **216**, 785 (1943). Delépine observed[3b] that Wurtz' "tricrotonylenamine" was the same as one of two conformational isomers (designated α and β) of composition $C_{12}H_{24}N_4$ that could be isolated, as hydrates, from the product of reaction of crotonaldehyde and aqueous ammonia at 0° to room temperature for 1–2 days, followed by heating on a water bath. Oxidation of the α isomer (the isomer isolated by Wurtz) with potassium permanganate, afforded an "anhydride" of β-aminobutyric acid in 7–8% yield.[3b] However, since neither the molecular weight of the "anhydride" nor the amount of β-aminobutyric acid released on hydrolysis was determined, the cyclic, trimeric structure of the anhydride was not unequivocably established.

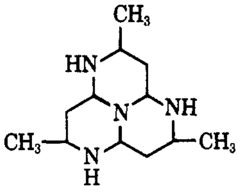
[4] A. Wurtz, *Compt. Rend.*, **88**, 940, 1154 (1879).



I



II



III

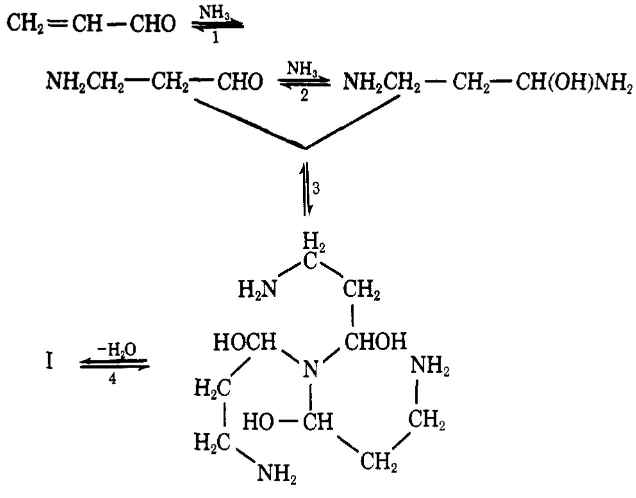
Reaction Conditions and Probable Course.—In the condensation of acrolein and ammonia to dodecahydro-1,4,7,9b-tetraazaphenalene (I), the best results were attained when the reactants in methanol were brought together at elevated temperature in the liquid phase, and a low concentration of acrolein relative to ammonia was maintained in the reactor at all times. The highest yields of I resulted from runs at about 150° and 1500 psi. Condensations maintained at about 100° afforded only a 50% yield of I; the yield of I was negligible when the reactants were mixed at 75° or below, even though finally heated to 150°. In all runs, acrolein appeared to be completely consumed regardless of temperature or contact time.

The acrolein–ammonia condensate I can be isolated by distillation at low pressure (when pure, it distils at about 117° at 0.1 mm), but degradation of nitrogen base by-products during distillation reduces the recovery of pure I. The purity of distilled product was increased by hydrogenation of the reaction mixture before distillation to eliminate unstable substances, but the yield of I was lowered by this procedure, possibly because of hydrogenolysis. The preferred method of isolating I was by solvent extraction of the crude reaction mixture after removal of the lower boiling components by vacuum distillation. This procedure afforded I as a buff-colored crystalline solid which, for highest purity, was sublimed under vacuum and recrystallized.

Methacrolein and crotonaldehyde were condensed with ammonia in the same manner as acrolein. The condensates, II and III, were isolated by Claisen distillation of the reaction mixture.

The mechanism of the formation of I has not been investigated, but certain experimental results are clues to the nature of the reaction. Two observations seem particularly relevant: reactions initiated between 100 and 150°, affording I, appear to take a basically different course from those initiated at lower temperatures; and the highest yields of I were obtained when ammonia was used in large excess. It seems reasonable to assume that the condensation leading to I is initiated by addition of ammonia to the ethylenic group, since this reaction is probably favored over carbonyl addition at the temperatures employed. Scheme I is a representation of the condensation consistent with these factors, and is in essence one of two mechanisms suggested by Delépine[3c] in explanation of the formation of Wurtz' "tricrotonylenamine" from crotonaldehyde and ammonia.

SCHEME I



The formation of I would be favored by the irreversibility of step 4 and also by high-reaction temperature. The large excess of ammonia that is maintained during the course of the reaction would promote the initial steps of the sequence, and would be expected to depress formation of another possible product, $N(CH_2CH_2CHO)_3$. Since it is not apparent that the latter could lead to I, its formation is probably minimal under reaction conditions affording the best yields of I.

As previously noted, acrolein was converted almost entirely to products other than I in runs carried out at temperatures of 75° or lower. Two explanations for this seem reasonable. Step 4 of the proposed mechanism may not proceed readily at the lower temperatures, in which case other reactions of the indicated intermediates may predominate; and condensations proceeding by addition of ammonia to the carbonyl group of acrolein, or merely catalyzed by ammonia, may assume increasing relative importance with decreasing temperature. Crotonaldehyde, in comparison with acrolein, is generally less reactive toward nucleophilic reagents, especially in respect to additions to the ethylenic group, and thus may be expected to behave somewhat differently in its reactions with ammonia. In Delépine's experiments,[3b] crotonaldehyde and aqueous ammonia afforded good yields of III even in experiments initiated at 0°, but it was necessary to heat the mixture for complete reaction.

Physical and Chemical Evidence for Structure I.—The assignment of the structure, dodecahydro-1,4,7,9b-tetraazaphenalene (I), to the acrolein–ammonia condensate, $C_9H_{18}N_4$, was based on chemical analyses, absorption spectral data, X-ray studies,[5] and the nature of the products obtained on reaction with mercuric acetate, on reaction with potassium permanganate, and on thermal degradation with palladium-on-carbon catalyst.

Potentiometric titration of $C_9H_{18}N_4$ in aqueous solution demonstrated the presence of three titratable amine group having pK'_a values of 7.6, 5.8, and 3.3. In the infrared spectrum, the number and sharpness of the intense bands in the 6.8–10.4-μ region are consistent with the compound being cyclic, but without five-membered rings. The lack of absorption in the 6.0–6.25-μ region indicates the absence of unsaturation either of the type C=C or C=N. The presence of a single NH stretching band in the 2.8–3.1-μ region shows that secondary but not primary amino groups are present.

The ultraviolet spectrum contained no absorption bands in the 200–400-μ range. This also is consistent

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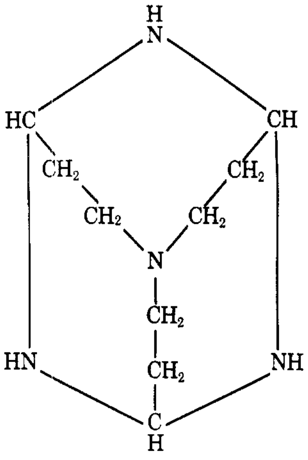
[5] A. E. Smith [*Acta Cryst.*, **19**, 248 (1965)] in concurrent studies established the structure of I by X-ray examination of the trishydrochloride salt.

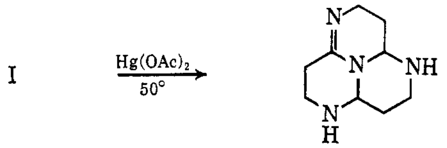
with the lack of C=C or C=N bonding. The failure of the compound to take up hydrogen in the presence of palladium-on-carbon catalyst confirmed the absence of unsaturation.



IV

The analytical and spectral data for $C_9H_{18}N_4$ are consistent with structure IV as well as that of I. Although the mass and nuclear magnetic resonance spectra were compatible with a cyclic structure, neither could be used to distinguish between I and IV. However, a preliminary X-ray examination of a hexagonal modification of the trishydrochloride salt rendered the cage structure IV improbable. Indeed, a detailed X-ray structure study that was later carried out with an orthorhombic modification of the hydrochloride showed that it possessed the flat, puckered configuration[5] I.

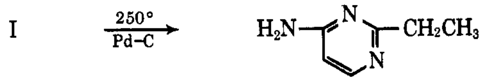
Oxidation of I with excess mercuric acetate in dilute aqueous acetic acid at 50° afforded a crystalline compound of two less hydrogen atoms in 44% yield.



V

The infrared spectrum of the product showed very intense absorption at 6.13 μ which is attributed to the presence of an amidine group.[6] The lack of any olefinic hydrogen resonance[7] at $\delta = 5.0$–5.5 ppm from tetramethylsilane in the nmr spectrum demonstrated the absence of carbon–carbon unsaturation. Mercuric acetate oxidations are known[8] to introduce double bonds allylic to tertiary nitrogen atoms. Secondary amines have been reported[9,10] to be unaffected by the reagent under the mild conditions employed here, although they may react[11] under more forcing conditions. Therefore, the spectral evidence for an amidine group in the oxidation product is also evidence against the proposed structure IV for the parent compound, since carbon–carbon unsaturation would be expected in the product from mercuric acetate oxidation of IV. On the other hand, the introduction of a carbon–nitrogen double bond is compatible with structure I, and accordingly, the oxidation product is assigned structure V.

Thermal degradation of I at 150–250° in the presence of 10% palladium-on-carbon catalyst afforded a new compound of composition $C_6H_9N_3$ (VI) in 57% yield. The proposed structure, 4-amino-2-ethylpyrimidine, was supported by chemical analyses and infrared, ultraviolet, and nmr spectral studies. The molecular weights obtained by titrimetric (125 ± 3, pK'_a 6.5 in water) and mass spectral (123) means were in excellent agreement. The infrared spectrum[11] in chloroform solution exhibited maxima at 2.81 and 2.91 (NH deformation of primary amine), 6.26 and 6.40 (aromatic skeletal vibrations), and 10.1 and 12.05 μ (ring vibrations). The ultraviolet absorption spectrum of VI showed maxima in 0.001 *N* sodium hydroxide solution at 232 mμ (*E* 11,200) and 270 (4400) which are similar to those of 232 (10,000) and 273 (5000) reported[12] for 4-amino-2,5-dimethylpyrimidine. In the nmr spectrum in deuteriochloroform solution, the triplet at $\delta = 1.28$ ppm and the quartet at $\delta = 2.72$ ppm ($J = 7.9$ cps) were ascribable to an ethyl group[13] attached to an aromatic ring. The chemical shifts [$\delta = 6.21$ (doublet) and 8.13 ppm (doublet)] and the coupling constant ($J = 6.1$ cps) of the pair of aromatic ring hydrogens were in reasonable agreement with those found by us for the corresponding hydrogens in 2-aminopyrimidine ($\delta = 6.56$ and 8.28 ppm, $J_{ortho} = 4.5$ cps). A broad NH_2 line at $\delta = 5.0$ ppm was identified by means of its downfield shift upon addition of formic acid. The structure of the pyrolysis product, thus established as 4-amino-2-ethylpyrimidine (VI), is consistent with a precursor having structure I and incompatible with a precursor having structure IV.



VI

Final chemical evidence for the structure of $C_9H_{18}N_4$ was obtained by oxidation under the conditions used by Delépine[3c] to oxidize the crotonaldehyde–ammonia condensate. Reaction of I with potassium permanganate in dilute alkaline solution at 0° resulted in an 11% conversion to a crystalline compound, $C_9H_{15}N_3O_3$. The assignment of structure VII, 1,5,9-triazacyclododecane-4,8,12-trione, to this compound was based on physical data and on the nature of the products obtained on hydrolysis and on reduction. The molecular weight, determined in aqueous solution with a Mechrolab vapor pressure osmometer (225), and also by mass spectroscopy (213), was clearly in accord with the cyclic tripeptide structure (mol wt 213) rather than that of a di- or tetrapeptide. The infrared spectrum (KBr) exhibited bands at 3.05, 6.08, and 6.45 μ characteristic of NH stretching and amide carbonyl absorption.[14] Hydrolysis of VII with aqueous hydrochloric

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(6) L. B. Bellamy, "Infrared Spectra of Complex Molecules," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1958, p 271.

(7) L. M. Jackman, "Nuclear Magnetic Resonance Spectroscopy," Pergamon Press Inc., New York, N. Y., 1959, p 61.

(8) N. J. Leonard, *et al.*, *J. Am. Chem. Soc.*, **77**, 439 (1955).

(9) N. J. Leonard and D. F. Morrow, *ibid.*, **80**, 371 (1958).

(10) R. Bonnett, W. M. Clark, A. Giddey, and Sir Alexander Todd, *J. Chem. Soc.*, 2087 (1959).

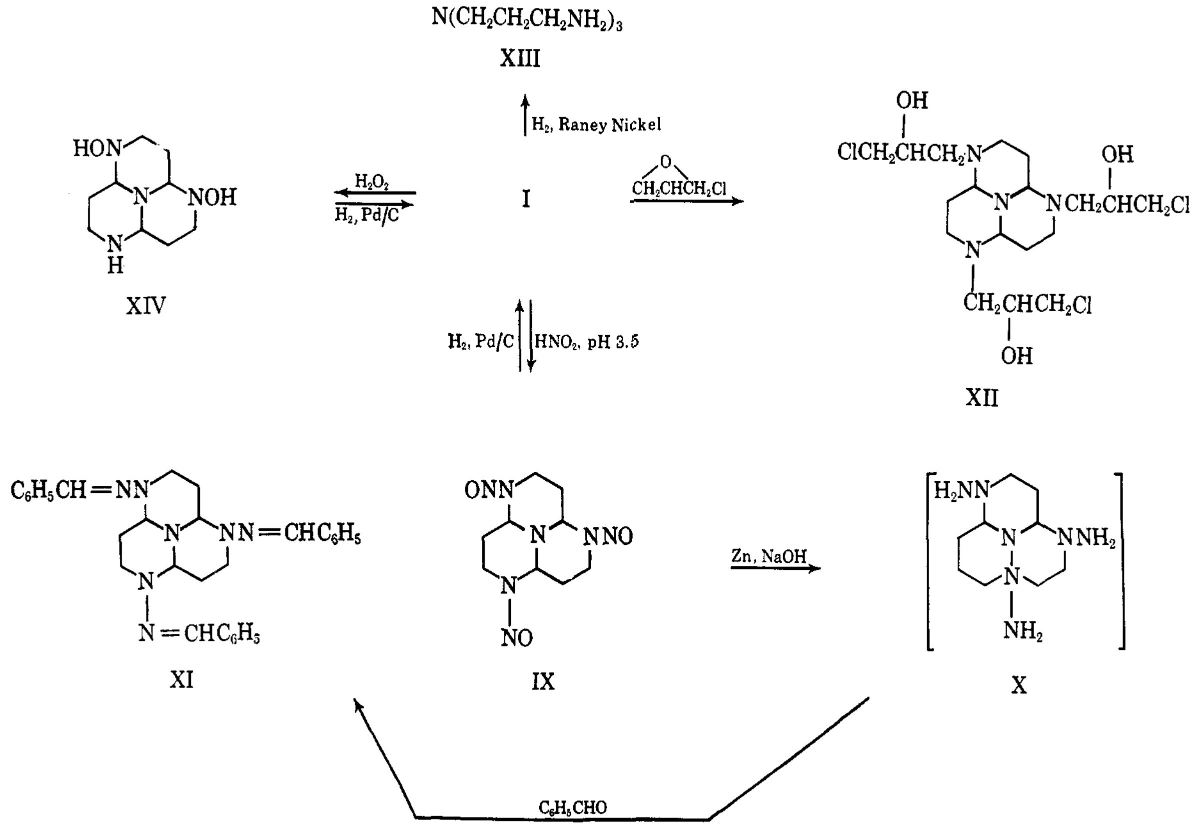
(11) Reference 6, pp 249 and 282.

(12) J. D. Barnhurst and D. J. Hennesy, *J. Am. Chem. Soc.*, **74**, 356 1952).

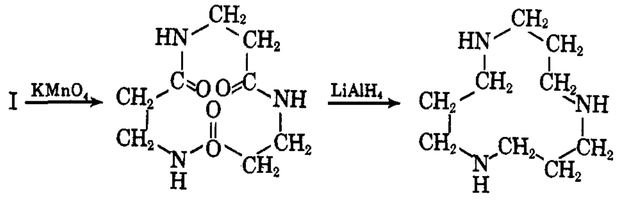
(13) Nmr Spectra Catalog, Vol. 1, Varian Associates, Palo Alto, Calif., 1962.

(14) Reference 6, p 205.

SCHEME II



acid at 110° afforded β-aminopropionic acid in 90% yield. Reduction with lithium aluminum hydride in refluxing tetrahydrofuran gave, in 30% yield, a trisamine whose elemental analysis, infrared spectrum, and molecular weight (see Experimental Section) were consistent with structure VIII, 1,5,9-triazacyclododecane. It seems evident that an oxidation product of structure VII could only arise from a precursor of structure I, and not from one of structure IV.



VII VIII

Reactions of Dodecahydro-1,4,7,9b-tetraazaphenalene (I).—The acrolein–ammonia condensate contains three secondary amine groups that are basic in character, and, indeed, in almost all reactions examined these three groups were involved. However, with one reagent, hydrogen peroxide, reaction with the third nitrogen was so slow that only the bis oxidation product was formed in sufficient quantity to be isolated.

Reaction of I with acetic anhydride in chloroform–pyridine solution afforded 1,4,7-triacetyldodecahydro-1,4,7,9b-tetraazaphenalene in 65% yield. Similarly, treatment of I with phenylisocyanate in tetrahydrofuran gave a tris(N-phenylcarbamyl) derivative in 56% yield. Chlorination in dilute sodium bicarbonate solution at 0° resulted in the consumption of 3 molar equiv of the bicarbonate. The insoluble crystalline product, presumed to be the tris(N-chloroamine), decomposed vigorously at 25° when dry.

Reaction with nitrous acid in aqueous solution at pH 3.5 gave 1,4,7-trinitrosododecahydro-1,4,7,9b-tetraazaphenalene (IX) in almost quantitative yield. This product was reconverted to I on hydrogenation with palladium-on-carbon catalyst, but was reduced to 1,4,7-triamino-1,4,7,9b-tetraazaphenalene (X) on treatment with zinc and aqueous sodium hydroxide. Although X was not stable enough to be isolated pure, it could be trapped as a tris(phenylhydrazone) (XI) in 34% yield (based on nitroso compound) by reaction with benzaldehyde.

Tris(3-chloro-2-hydroxypropyl)dodecahydro-1,4,7,9b-tetraazaphenalene (XII) was obtained in 70% yield on reaction of I with epichlorohydrin in methanol at 30°. The structure of XII was evident from elemental analysis and quantitative determination of easily saponifiable chlorine. Treatment of XII with powdered sodium hydroxide in methyl ethyl ketone as diluent at 50° gave a compound whose oxirane oxygen content was about 50% of theory for triglycidyldodecahydro-1,4,7,9b-tetraazaphenalene. This epoxy compound polymerized in chloroform solution during several weeks at room temperature.

Hydrogenolysis of I with Raney nickel catalyst in tetrahydrofuran–ammonia solution at 140–150° under 3200 psi of hydrogen pressure afforded two polyamines, both of molecular composition $C_9H_{24}N_4$. These products, which were separated by fractional distillation, were formed in 32 and 16% yield. No attempt was made to identify the compound formed in lower yield. Although the higher yield compound XIII could not be obtained in a completely pure state (only 90%), it was identified as tris(γ-aminopropyl)amine by conversion to a tris(phenylthiourea) derivative. The melting point of the latter compound was not depressed on admixture with a sample of the tris(phenylthiourea) derivative of authentic tris(γ-aminopropyl)amine.

Authentic XIII[15] was prepared in 45% yield by hydrogenation of tris(β-cyanoethyl)amine with Raney nickel catalyst at 115–120° in tetrahydrofuran–ammonia solution. The latter compound was obtained in 80% yield by reaction of acrylonitrile with ammonia in water at 85°. The procedure (see Experimental Section) resulted in a markedly higher yield of tris(β-cyanoethyl)amine than has been previously reported (40%).[16]

Efforts to quaternize the central, bridgehead nitrogen of I with methyl iodide were unsuccessful. The only product obtained was a small amount of a compound that resulted from alkylation of one of the peripheral nitrogens. The failure of 1,4,7-triacetyl-dodecahydro-1,4,7,9b-tetraazaphenalene to react with methyl iodide confirmed the lack of reactivity of the bridgehead nitrogen.

Oxidation of I (Scheme II) with hydrogen peroxide was carried out in aqueous solution at ambient pH, 9.5, and 25–30°. The first molar equivalent of hydrogen peroxide was consumed within 6 hr, and the second one only after 72 hr. Work-up afforded a 56% yield of a product containing two oxygen atoms. Reconversion of this product to I (70% yield) by hydrogenation in the presence of palladium-on-carbon catalyst showed that the cyclic structure had remained intact. The product was assigned a bis(hydroxylamine) structure (XIV), since the bridgehead tertiary nitrogen appears in other reactions to be unreactive. Secondary amines have been reported[17] to be oxidized to N,N-disubstituted hydroxylamines with hydrogen peroxide.

Experimental Section

Apparatus and Reagents.—The reactor was a 1150-ml, horizontally stirred, Hastelloy-B autoclave equipped with an internal heating coil, a thermometer well, and two ports on opposite sides for charging reactants. Operation was under hydrostatic conditions and product take-off through a water-cooled condenser was from the top of the vessel. The pressure of the system was controlled by a dome-loaded valve connected to the take-off condenser. The latter was connected also to a pressure gauge, 3000-psi bursting disk, 2000-psi working pressure relief device, vent, and high-pressure nitrogen source. Reactants were pumped into the system.

The acrolein, methacrolein, and crotonaldehyde were distilled before use and inhibited with 0.1 (wt %) hydroquinone. The distilled acrolein was shown by gas–liquid partition chromatography to contain 93% acrolein, 3.1% water, 1.2% acetone, and small amounts of aldehydic and alcoholic impurities.

Reaction of Acrolein and Ammonia.—In a typical high-yield experiment, the 1150-ml reactor was charged liquid full with a 51 wt% solution of ammonia in methanol. While continuing to pump solution through the vessel, the reactor was brought to a temperature of about 150° and pressured to 1500 psi with nitrogen. Under these conditions, the reactor content was liquid and consisted of approximately 318 g of ammonia and 306 g of methanol. When the system had reached equilibrium, a 49.7 wt % solution of acrolein in methanol was pumped into the reactor through one port and ammonia through the other (feed time, 271 min). The reaction temperature was maintained at 148–151° and the pressure in the range from 1400 to 1500 psi. A total of 528 g (8.78 moles) of acrolein and about 1438 g (84.5 moles) of ammonia (including the precharge) were added to the reactor.

At the conclusion of the run, the continuously removed product and the reactor content were combined and immediately stripped under vacuum to remove unreacted ammonia, methanol, and other volatiles, leaving 570 g of a brown, crystalline solid, melting over the range 100–110°. This material was extracted six times with refluxing cyclohexane, 2800 ml of solvent being used in the first extraction. Cooling the extract to 10° and filtering afforded a total of 516 g of buff-colored crystalline solid, mp 115–120° (at 90% purity, 87% yield[18] based on acrolein charged). Recrystallization of a portion of the solid from carbon tetrachloride, followed by vacuum sublimation, gave white, needle-like crystals, mp 118–120°, bp 117° (0.1 mm).

Anal. Calcd for $C_9H_{18}N_4$: C, 59.3; H, 9.9; N, 30.7; total basic N, 1.65 equiv/100 g; mol wt, 182. Found: C, 59.2; H, 10.1; N, 30.2; total basic N, 1.66 equiv/100 g; mol wt (ebullioscopic in ethanol), 182. The infrared spectrum showed absorption in the region 2.8–3.1 μ (NH stretching), 13 sharp bands of medium to strong intensity in the region 6.8–10.4 μ, and no absorption band in the 6.0–6.25-μ region (no C=C or C=N).

Reaction of Methacrolein and Ammonia.—The reactor was charged with 250 g (14.7 moles) of ammonia and 200 ml of methanol, heated to 150°, and pressured to 1500 psi. Into the ports of the reactor were simultaneously pumped a solution of 352 g (5.03 moles) of methacrolein in 286 g (8.94 moles) of methanol and 1340 g (78.8 moles) of ammonia (feed time, 70 min). Product take off began when the reactor became liquid full. The reaction mixture was maintained at 149–156° and 1325–1525 psi. When all of the reagents had been added, the reactor content was combined with product already taken off and allowed to stand at ambient temperature until most of the unreacted ammonia had evolved. The product mixture was then treated with hydrogen for 1 hr at 84–100° and 1000–1130 psi using Raney nickel catalyst; 0.49 mole of hydrogen was absorbed/mole of methacrolein charged. Claisen distillation afforded 186 g (49% yield on aldehyde charged) of viscous, yellow liquid distilling at 103–121° (<0.1 mm). A heart cut, bp 115–117° (<0.1 mm), was analyzed.

Anal. Calcd for $C_{12}H_{24}N_4$: C, 64.3; H, 10.7; N, 25.0; mol wt, 224. Found: C, 64.0; H, 11.1; N, 24.2; mol wt (ebullioscopic in ethanol), 215. The infrared spectrum showed a singlet at 2.8–3.1 μ (NH stretching) and no absorption in the region of 6.0–6.25 μ (no C=C or C=N).

Reaction of Crotonaldehyde and Ammonia.—This reaction was carried out in the same manner as that of methacrolein and ammonia. The precharge to the reactor was about 250 g (14.8 moles) of ammonia in 200 ml of methanol. The reactant feeds consisted of 704 g (10.06 moles) of crotonaldehyde in 730 g of methanol, and 2061 g (121.3 moles) of ammonia (feed time, 140 min). The reaction mixture was maintained at 149–151° and 1400–1550 psi. The crude reaction product after evolution of ammonia at room temperature, was treated with hydrogen for 1 hr at 99–110° and 755–1257 psi using Raney nickel catalyst; 0.107 mole of hydrogen was absorbed/mole of crotonaldehyde charged. After removal of volatiles by distillation (to 100° under reduced pressure), 701 g of a viscous, yellow liquid remained. Claisen distillation gave 653 g (87% yield) of a nearly water white, viscous liquid distilling over the range 119 (0.9 mm)–129° (0.1 mm). A heart cut, boiling at 127–128° (0.1 mm), was analyzed.

Anal. Calcd for $C_{12}H_{24}N_4$: C, 64.3; H, 10.7; N, 25.0; mol wt, 224. Found: C, 64.4; H, 11.0; N, 24.6; mol wt (ebullioscopic in ethanol), 220; mol wt (mass spectroscopy), 224. The infrared absorption spectrum showed a singlet at 2.8–3.1 μ (NH stretching) and no absorption at 6.0–6.25 μ (no C=C or C=N).

In another preparation of the III adduct, 704 g (10.06 moles) of crotonaldehyde in 730 g of methanol and 2166 g (127.5 moles) of ammonia were pumped into the reactor (precharged as previously) at approximately the same rates as before (feed time,

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[15] O. F. Wiedeman and W. H. Montgomery, *J. Am. Chem. Soc.*, **67**, 1994 (1945).

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[18] R. C. Hurlbert of this laboratory has recently observed that high yields of this product are most consistently obtained by the addition of a trace of sulfuric acid (0.001 mole/mole of acrolein) to the methanol–acrolein feed.

147 min). After distillation, to remove ammonia and other volatiles, 735 g of a viscous brown liquid remained. Claisen distillation gave 706 g (94% yield) of product as a viscous, pale yellow liquid.

Some distilled fractions of these crotonaldehyde–ammonia condensates on standing crystallized to needles, mp 40–50°.

Acetylation of I.—Acetic anhydride (30.7 g, 0.3 mole) was added dropwise over a 30-min period to a stirred solution of dodecahydro-1,4,7,9b-tetraazaphenalene (18.2 g, 0.1 mole) and pyridine (23.8 g, 0.3 mole) in 175 ml of chloroform at 20–25°. Stirring was continued at 25° for 4 hr, when the solution was washed with 10% sodium bicarbonate and dried. Removal of the solvent under vacuum gave 20 g (65% yield) of white crystals which melted at 220–222° after recrystallization from ethanol.

Anal. Calcd for $C_{15}H_{24}N_4O_3$: C, 58.3; H, 7.8; N, 18.2. Found: C, 58.0; H, 7.9; N, 17.8.

Reaction of I with Phenyl Isocyanate.—Phenyl isocyanate (18.0 g, 0.15 mole) was added dropwise over a 30-min period to a stirred solution of I (9.1 g, 0.05 mole) in 100 ml of tetrahydrofuran at 25–30°. Stirring was continued at 25° for 4 hr. The white crystals which separated were collected and washed with tetrahydrofuran. Recrystallization from acetone afforded 15 g (56% yield) of white plates, mp 167–170°.

Anal. Calcd for $C_{30}H_{33}N_7O_3$: C, 66.7; H, 6.1; N, 18.1. Found: C, 66.4; H, 6.3; N, 17.9.

Chlorination of I.—Chlorine was bubbled into a stirred solution of I (9.1 g, 0.05 mole) and sodium bicarbonate (42 g, 0.5 mole) in 400 ml of water at 10° at a rate slightly in excess of that at which it was absorbed. Stirring was continued at 5–10° for 10 hr, at which time 0.15 mole of sodium bicarbonate had been consumed. The white crystals were collected and washed with fresh water. The product (20 g, wet weight) decomposed to an orange oil when dried in a vacuum oven at 25°.

Oxidation of I with Hydrogen Peroxide.—A solution of I (18.2 g, 0.1 mole) and 30% H_2O_2 (23 g, 0.2 mole) in 125 ml of water was stirred at 25–30° at ambient pH 9.5 for 72 hr, at which time 90% of the peroxide had been consumed. The residual peroxide was decomposed with 10% palladium on carbon and the water removed by vacuum distillation. The residual liquid was taken up in chloroform, dried, and concentrated under vacuum to give 24 g of white semicrystalline residue. Recrystallization from 50% *n*-hexane–chloroform afforded 12 g (56% yield) of XIV as white crystals which decomposed when heated to 240°.

Anal. Calcd for $C_9H_{18}N_4O_2$: C, 50.3; H, 8.4; N, 26.2. Found: C, 50.1; H, 8.4; N, 26.8.

Hydrogenation of XIV.—A mixture of 1.7 g (0.008 mole) of XV, 0.5 g of 10% palladium-on-carbon catalyst, and 20 ml of ethanol shaken at 25° under 40-psi hydrogen pressure absorbed 2.2 molar equiv of hydrogen in 6 hr. The reaction mixture was filtered and the filtrate was dried and concentrated to give a pale yellow crystalline residue. Vacuum sublimation at 105° afforded 1.0 g (70% yield) of white crystals, mp 115–118°, whose infrared spectrum in carbon tetrachloride solution was identical with that of I.

Oxidation of I with Mercuric Acetate.—A solution of I (12.8 g, 0.07 mole) and mercuric acetate (100 g, 0.3 mole) in 50 ml of 5% aqueous acetic acid (pH 4.0) was stirred at 30° for 3 hr and then at 55° for 3 hr. The mixture was filtered to remove mercurous acetate (35 g, 95% of theory for removal of two hydrogen atoms) and the filtrate saturated with hydrogen sulfide. After filtration the solution was neutralized with sodium bicarbonate and concentrated to a volume of 50 ml by vacuum distillation. To this residual liquid was added 150 ml of 40% sodium hydroxide. Multiple extraction with chloroform gave V (5.5 g, 44% yield) as white crystals which melted at 118–120° after sublimation *in vacuo*.

Anal. Calcd for $C_9H_{16}N_4$: C, 60.0; H, 8.9; N, 31.2; mol wt, 180. Found: C, 60.2; H, 9.1; N, 30.8; mol wt (mass spectroscopy), 180.

Nitrosation of I.—Enough dilute hydrochloric acid was added dropwise to a stirred solution of I (18.2 g, 0.1 mole) and sodium nitrite (28 g, 0.4 mole) in 400 ml of water at 5° to maintain the pH at 3.5. Stirring was continued at 15–20° at pH 3.5 for 2 hr. The precipitated product, collected and washed with cold water (26 g, 96% yield), was dried at 110° and 1-mm pressure overnight. Recrystallization from acetonitrile gave IX as pale yellow crystals which decomposed at 230°.

Anal. Calcd for $C_9H_{15}N_7O_3$: C, 40.2; H, 5.6; N, 36.4. Found: C, 39.9; H, 5.6; N, 36.7.

Hydrogenation of Nitrosation Product (IX).—Hydrogenation of IX (5.4 g, 0.02 mole) in 150 ml of water with 2 g of 10% palladium-on-carbon catalyst proceeded at 25° and 50-psi pressure with absorption of 6.2 mole equiv of hydrogen over a 2-hr period. Catalyst was removed by filtration and water by distillation under reduced pressure. The solid residue was sublimed and then recrystallized from *n*-hexane–chloroform to afford 2.4 g (67% yield) of I, mp 115–118°.

Reduction of Nitrosation Product (IX) with Zinc and Sodium Hydroxide.[19]—A mixture of IX (13.5 g, 0.05 mole), zinc dust (60 g), and 600 ml of 10% sodium hydroxide was stirred at 20–25° for 40 hr. The unreacted zinc dust was removed by filtration.

To the filtrate, neutralized to pH 7.0 with 20% sulfuric acid, was added a solution of benzaldehyde (18.8 g, 0.2 mole) in 250 ml of ethanol. The resulting mixture was made slightly acidic (pH 5.0) with 20% sulfuric acid and stirred at 25–30° for 3 hr. The crystals which separated were collected and washed with 50% ethanol. The product was triturated with hot chloroform and filtered. Removal of the chloroform from the filtrate gave 8.3 g (34% yield) of white crystals, mp 201–204°. Recrystallization from *n*-hexane–chloroform gave purified XI, mp 209–210°, which was vacuum dried over phosphorus pentoxide at 110°.

Anal. Calcd for $C_{30}H_{33}N_7$: C, 73.2; H, 6.8; N, 20.9. Found: C, 72.9; H, 6.7; N, 19.9.

Oxidation of I with Alkaline Potassium Permanganate.—A solution of potassium permanganate (74.3 g, 0.47 mole) in 200 ml of water was added rapidly to a stirred solution of I (36.4 g, 0.2 mole) and potassium hydroxide (16 g, 0.285 mole) in 700 ml of water at −5–0°. Stirring was continued at 0° for 30 min. Manganese dioxide was removed by filtration and washed several times with hot water. The filtrate was neutralized with carbon dioxide and water was removed on a rotary evaporator under vacuum. The residual solid was leached with six 300-ml portions of hot 95% ethanol.

The ethanol was removed by vacuum distillation and the solid residue crystallized from 30 ml of water. The white crystals which separated were collected and washed with cold water and then cold ethanol. More of this product (total of 4.5 g, 11% yield) was obtained by repeating this procedure. After an additional recrystallization from water, VII (mp >300°) was dried *in vacuo* over phosphorus pentoxide at 100°.

Anal. Calcd for $C_9H_{15}N_3O_3$: C, 50.6; H, 7.1; N, 19.8, mol wt, 213. Found: C, 50.9; H, 7.2; N, 20.0; mol wt (Mass spectroscopy), 213.

Hydrolysis of VII with Hydrochloric Acid.—A solution of VII (1.0 g, 0.005 mole) in 10 ml of 20% hydrochloric acid was maintained at 110° for 5 hr. Excess acid and solvent were removed by distillation under reduced pressure. The residue, dissolved in 30 ml of water, was stirred with silver oxide (4 g) for 18 hr. Solids were removed by filtration and the filtrate was saturated with hydrogen sulfide. After treatment of the aqueous solution with decolorizing charcoal and removal of water, the solid residue was recrystallized from 90% ethanol to afford 1.2 g (90% yield) of β-aminopropionic acid, mp 193–194°. The melting point of an admixture with an authentic sample was undepressed.

Anal. Calcd for $C_3H_7NO_2$: C, 40.5; H, 7.9; N, 15.7. Found: C, 40.8; H, 8.0; N, 15.3.

Reduction of VII with Lithium Aluminum Hydride.—A mixture of VII (4.1 g, 0.02 mole) and lithium aluminum hydride (3.8 g, 0.1 mole) in 700 ml of tetrahydrofuran was stirred at 68° for 20 hr. Water (0.4 mole) was added dropwise to the mixture which was then stirred at 25° for 2 hr. Solids were removed by filtration and washed several times with both tetrahydrofuran and chloroform. Distillation of the residual liquid after removal of the solvent gave 2.0 g, bp 60–72° (1 mm). Fractional distillation of the product through a microspinning-band column afforded VIII as a center cut, 1.0 g (29% yield), bp 77–78° (3 mm).

Anal. Calcd for $C_9H_{21}N_3$: C, 63.1; H, 12.3; N, 24.6; mol wt, 171. Found: C, 62.5; H, 12.1; N, 23.8; mol wt, 171 (94% pure by mass spectroscopy). The infrared spectrum exhibited a band at 3.07 μ (NH stretch) which is the same as the spectrum reported[20] recently for 1,4,7,10-tetraazacyclododecane.

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Thermal Degradation of I with Pd–C Catalyst.—A mixture of dodecahydro-1,4,7,9b-tetraazaphenalene (15.5 g, 0.085 mole) and 10% palladium on carbon (3 g) in a round-bottom flask began to evolve gaseous products when heated by an oil bath to 135°. The bath temperature was gradually raised during a 90-min period until a final temperature of 250° was obtained. The reaction mixture was diluted with 100 ml of hot water and filtered to remove catalyst. Evaporation of the water at 100° and reduced pressure left a residue which was leached with carbon tetrachloride. Two sublimations of the insoluble material at 100–150° and 0.5-mm pressure gave 6.0 g (57% yield) of pale yellow crystals, mp 172–176°. After an additional sublimation and a recrystallization from chloroform, 4-amino-2-ethylpyrimidine was obtained as white plates, mp 184–185°.

Anal. Calcd for $C_6H_9N_3$: C, 58.5; H, 7.37; N, 34.1; mol wt, 123. Found: C, 58.2; H, 7.50; N, 33.6; mol wt (mass spectroscopy), 123.

Evaporation of the carbon tetrachloride extract followed by sublimation at reduced pressure afforded a purple substance melting at 95–96° and of approximate composition $C_9H_8N_4$ (21% yield).[21]

Reaction of I with Epichlorohydrin.—A solution of I (9.1 g, 0.05 mole) and epichlorohydrin (14 g, 0.15 mole) in 50 ml of methanol was stirred at 25° for 18 hr. Volume reduction on a rotary evaporator at 40° and low pressure afforded 21 g of pale yellow solid. The product was triturated with hot chloroform and filtered to remove insoluble material. The chloroform solution was evaporated at reduced pressure to give 16 g (70% yield) of a glass (XII).

Anal. Calcd for $C_{18}H_{33}Cl_3N_4O_3$: C, 46.9; H, 7.19; Cl, 23.2; N, 12.2; chlorohydrin value, 0.65 equiv/100 g. Found: C, 46.2; H, 7.09; Cl, 23.9; N, 12.0; chlorohydrin value, 0.64 equiv/100g.

Reaction of XII with Sodium Hydroxide.—A solution of XII (7.4 g, 0.02 mole) in 75 ml of methyl ethyl ketone was stirred for 2 hr at 50° with powdered sodium hydroxide (3 g, 0.075 mole). The mixture was filtered and the filtrate was neutralized with Dry Ice. After drying, volume reduction on a rotary evaporator at 40° and low pressure gave 5 g (85% yield) of a pale yellow syrup which was soluble in most organic solvents.

Anal. Calcd for $C_{18}H_{30}N_4O_3$: epoxide value, 0.86 equiv/100 g. Found: epoxide value, 0.43 equiv/100 g.

Preparation of Tris(β-cyanoethyl)amine.—Acrylonitrile (110 g, 2 moles) was added dropwise to a stirred solution of 28% ammonium hydroxide (61 g, 1 mole) at 30° at such a rate that little or no second phase was present at any time. Stirring was continued for 2 hr at 30° and then water (350 ml) and more acrylonitrile (110 g, 2 moles) were added. After the mixture stirred at 75–80° for 48–60 hr, water and excess acrylonitrile were removed by distillation under reduced pressure. The residual liquid (140 g, 80% yield) crystallized on standing, mp 48–54°. Recrystallization from ethanol gave white needles, mp 58–59°.

Preparation of Tris(γ-aminopropyl)amine.—A mixture of tris(β-cyanoethyl)amine (35 g, 0.2 mole), ammonia (20 g), Raney nickel (5 g), and tetrahydrofuran (250 ml), shaken in a 700-ml rocking autoclave at 115–120° under 3200-psi hydrogen pressure, absorbed 5.8 mole equiv of hydrogen in 15 hr. The reaction mixture was diluted with chloroform and filtered. Drying and removal of the solvent under reduced pressure gave 24 g of pale yellow liquid which distilled at 65–120° (0.1 mm). Fractional distillation through a Piros–Glover spinning-band column at 1.5-mm pressure gave the following: fraction 1, 3.5 g, bp 75–78°; fraction 2, 2.5 g, bp 79–133°; and fraction 3, tris(γ-aminopropyl)amine, 16 g, bp 134–135° (44% yield), $n^{25}D$ 1.4898 (fraction 3).

Anal. Calcd for $C_9H_{24}N_4$: C, 57.5; H, 12.8; N, 29.8; basic N, 29.8. Found (fraction 1): C, 56.9; H, 12.9; N, 29.4. Found (fraction 3): C, 57.7; H, 13.0; N, 29.4; basic N, 29.8.

Tris(γ-aminopropyl)amine with Phenyl Isothiocyanate.—A mixture of phenyl isothiocyanate (1.5 g) and tris(γ-aminopropyl)amine (0.5 g) reacted exothermally with solidification to a crystalline mass. The solid was powdered and washed with *n*-hexane and then 50% ethanol. After two recrystallizations from ethanol the product, which was dried *in vacuo* over phosphorus pentoxide at 78°, melted at 92–95°.

Anal. Calcd for $C_{30}H_{39}N_7S_3$: C, 60.6; H, 6.6; N, 16.5; S, 16.2. Found: C, 59.9; H, 6.4; N, 16.4; S 16.2.

Hydrogenolysis of I.—A mixture of purified I (36.4 g, 0.2 mole), ammonia (20 g), Raney nickel (12 g), and tetrahydrofuran (150 ml) shaken in a 700-ml rocking autoclave at 145–150° under 3200-psi hydrogen pressure absorbed 2.8 mole equiv of hydrogen in 18 hr. The reaction mixture was diluted with chloroform and filtered. After drying and removal of the solvent under reduced pressure, distillation gave 21 g of pale yellow liquid, bp 50–110° (0.1 mm). Fractional distillation through a Piros–Glover spinning-band column at 1.5-mm pressure afforded the following: fraction 1, 6.0 g, bp 75–77°; fraction 2, 2.0 g, bp 78–135°; and fraction 3, 12 g, bp 135–138° (32% yield), $n^{25}D$ 1.4910 (fraction 3).

Anal. Calcd for $C_9H_{24}N_4$: C, 57.5; H, 12.8; N, 29.8; basic N, 29.8; mol wt, 188. Found (fraction 1): C, 56.9; H, 13.1; N, 30.0; basic N, 29.3; mol wt (mass spectroscopy), 188. Found (fraction 3): C, 57.6; H, 12.9; N, 29.3; basic N, 29.0; mol wt (mass spectroscopy), 188.

Hydrogenolysis Product XIII with Phenyl Isothiocyanate.—A mixture of phenyl isothiocyanate (1.5 g) and XIII (0.5 g) reacted exothermally with solidification to a crystalline mass. The solid was powdered and washed with *n*-hexane and then 50% ethanol. After two recrystallizations from ethanol the product, which was dried *in vacuo* over phosphorus pentoxide at 78°, melted at 94–97°. Further recrystallization did not change the melting point. An admixture with an authentic sample of the tris(γ-aminopropyl)amine phenyl isothiocyanate derivative melted at 93–97°.

Anal. Calcd for $C_{30}H_{39}N_7S_3$: C, 60.6; H, 6.6; N, 16.5; S, 16.2. Found: C, 61.0; H, 6.6; N, 16.1; S, 16.6.

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(21) This compound has been tentatively identified as 1,4,7,9b-tetraazaphenalene [J. L. Winkle, U. S. 3,112,314 (Nov 26, 1963)].