CONDENSATION OF ALICYCLIC KETONES WITH UREA AND THIOUREA

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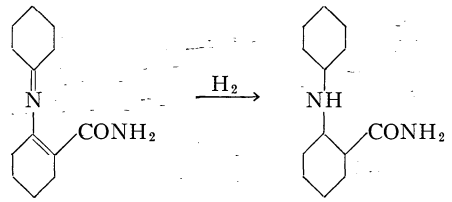
ABSTRACT

The previous assignment of a cis conformation to cyclohexyl 2-carbamylcyclohexylamine, which was prepared by the condensation of urea with cyclohexanone, has been confirmed by equilibration in the presence of potassium *t*-butoxide. The failure of 4-*t*-butylcyclohexyl 2-carbamyl-4-*t*-butylcyclohexylamine to equilibrate under the same conditions is discussed in relation to its structure. 1,2,3,4,5,6,7,8-Octahydroacridine was prepared by the condensation of 2,2′-methylene-bis-cyclohexanone with urea.

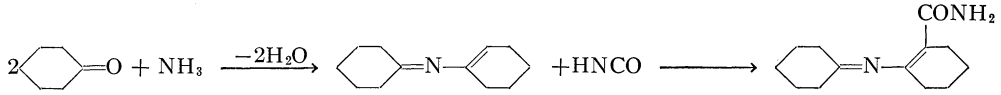
The product from the condensation of cyclohexanone with urea in alkaline medium was assigned (1) structure I on the basis of its analysis, infrared spectrum, and hydrogenation to cyclohexyl 2-carbamylcyclohexylamine (II). Later Scarborough and Gould



I II

(2) reported an improved procedure for the preparation of compound I. During the present investigation a new process (cf. Experimental) was developed which gives high yields of this condensation product. The latter procedure was used in the preparation of the compounds listed in Table I. Cyclohexylidene 2-thiocarbamylcyclohex-1-enylamine was prepared from the condensation of cyclohexanone with thiourea. The infrared and ultraviolet absorption bands listed in Tables II and III respectively show that these condensation products have the same general structure. If the imino nitrogen in structure I is assumed to be equivalent to carbon for calculating the ultraviolet absorption maximum then the calculated (3) value of 308 mμ is in good agreement with the observed value of 305 mμ (Table III).

Cyclohexylidene 2-carbamylcyclohex-1-enylamine (I) was considered (1) to be formed by the carbamylation of an enamine intermediate and the reaction sequence may be represented as follows:



The previous (1) scheme showed the addition of HNCO to 1-aminocyclohexene instead of cyclohexylidene cyclohex-1-enylamine. Isocyanic acid would be expected to add more readily to the latter compound because of its closer structural relationship to typical

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TABLE I

Alicyclic ketone – urea and – thiourea condensation products

Compound	M.p., °C (dec)	Yield, %	Formula	Carbon %		Hydrogen %		Nitrogen %	
				Calc.	Found	Calc.	Found	Calc.	Found
Cyclopentylidene 2-carbamylcyclopent-1-enylamine	237–238*,†	11	$C_{11}H_{16}N_2O$	68.71	68.69	8.39	8.39	14.58	14.95
4-Methylcyclohexylidene 2-carbamyl-4-methylcyclohex-1-enylamine	207‡	70§	$C_{15}H_{24}N_2O$	72.54	72.39	9.74	9.50	11.28	11.29
4-*t*-Butylcyclohexylidene 2-carbamyl-4-*t*-butylcyclohex-1-enylamine	274–275†	47‖	$C_{21}H_{36}N_2O$	75.86	76.12	10.91	11.08	8.42	8.44
Cyclohexylidene 2-thiocarbamylcyclohex-1-enylamine	218–222‡	87‖	$C_{13}H_{20}N_2S$	66.05	65.80	8.53	8.37	11.85	11.54¶
4-Methylcyclohexylidene 2-thiocarbamyl-4-methylcyclohex-1-enylamine	257–258‡	40‖	$C_{15}H_{24}N_2S$	68.13	68.05	9.15	9.42	10.59	10.61**

*Melting points vary with rate of heating. Decomposition points as high as 246° have been recorded for this compound in evacuated tubes.
†Crystallized from ethanol.
‡From aqueous methanol.
§Method A.
‖Method B.
¶Sulphur, Calc.: 13.57%. Found: 13.70%.
**Sulphur, Calc.: 12.12%. Found: 12.19%.

TABLE II

Infrared absorption band (cm^{-1}) assignments*

Compound	Stretching modes		Bending modes
	N—H	C=O	N—H
Cyclopentylidene 2-carbamylcyclopent-1-enylamine	3260	1610	1545
Cyclohexylidene 2-carbamylcyclohex-1-enylamine	3280, 3160	1625	1525
4-Methylcyclohexylidene 2-carbamyl-4-methylcyclohex-1-enylamine	3390, 3260	1620	1512
4-*t*-Butylcyclohexylidene 2-carbamyl-4-*t*-butylcyclohex-1-enylamine	3300, 3235, 3180	1615	1607, 1518
Cyclopentyl 2-carbamylcyclopentylamine hydrochloride	3325, 3125	1662	1580
Cyclohexyl 2-carbamylcyclohexylamine (m.p. 128°)	3325, 3260, 3140	1665	1580
Cyclohexyl 2-carbamylcyclohexylamine (m.p. 75–95°)	3445, 3340, 3280, 3195	1680	1610
4-Methylcyclohexyl 2-carbamyl-4-methylcyclohexylamine hydrochloride	3320, 3140	1663	1605
4-*t*-Butylcyclohexyl 2-carbamyl-4-*t*-butylcyclohexylamine	3275, 3100	1655	1580
Cyclohexyl 2-carbamylcyclohexylnitrosamine (m.p. 167°)	3425, 3325, 3215	1680	1625
Cyclohexyl 2-carbamylcyclohexylnitrosamine (m.p. 158°)	3380, 3200	1666, 1685	1632

*Infrared spectra were determined on Nujol mulls of the crystalline compounds. A Perkin–Elmer model 21 spectrometer was used.

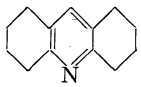
TABLE III
Ultraviolet absorption*

Compound	λ_{max} (mμ)	ϵ_{max}
Cyclopentylidene 2-carbamylcyclopent-1-enylamine	306.5	6350
	220	End absorption
Cyclohexylidene 2-carbamylcyclohex-1-enylamine	305	6720
	220	End absorption
4-Methylcyclohexylidene 2-carbamyl-4-methylcyclohex-1-enylamine	305	6350
	220	End absorption
4-*t*-Butylcyclohexylidene 2-carbamyl-4-*t*-butylcyclohex-1-enylamine	306	2000
Cyclohexylidene 2-thiocarbamylcyclohex-1-enylamine	377	1800
	279.5	4950
	215	End absorption

*The ultraviolet spectra were determined on ethanolic solutions of the compounds with a Beckman DK–1 recording spectrophotometer.

enamines. Some evidence in support of the prior condensation of two more equivalents of cyclohexanone with ammonia is provided by the following observation.

An attempt to form a carbamyl derivative of 2,2′-methylene-bis-cyclohexanone under the conditions used for the preparation of cyclohexylidene 2-carbamylcyclohex-1-enylamine gave the known (4, 5) 1,2,3,4,5,6,7,8-octahydroacridine (III). This new method

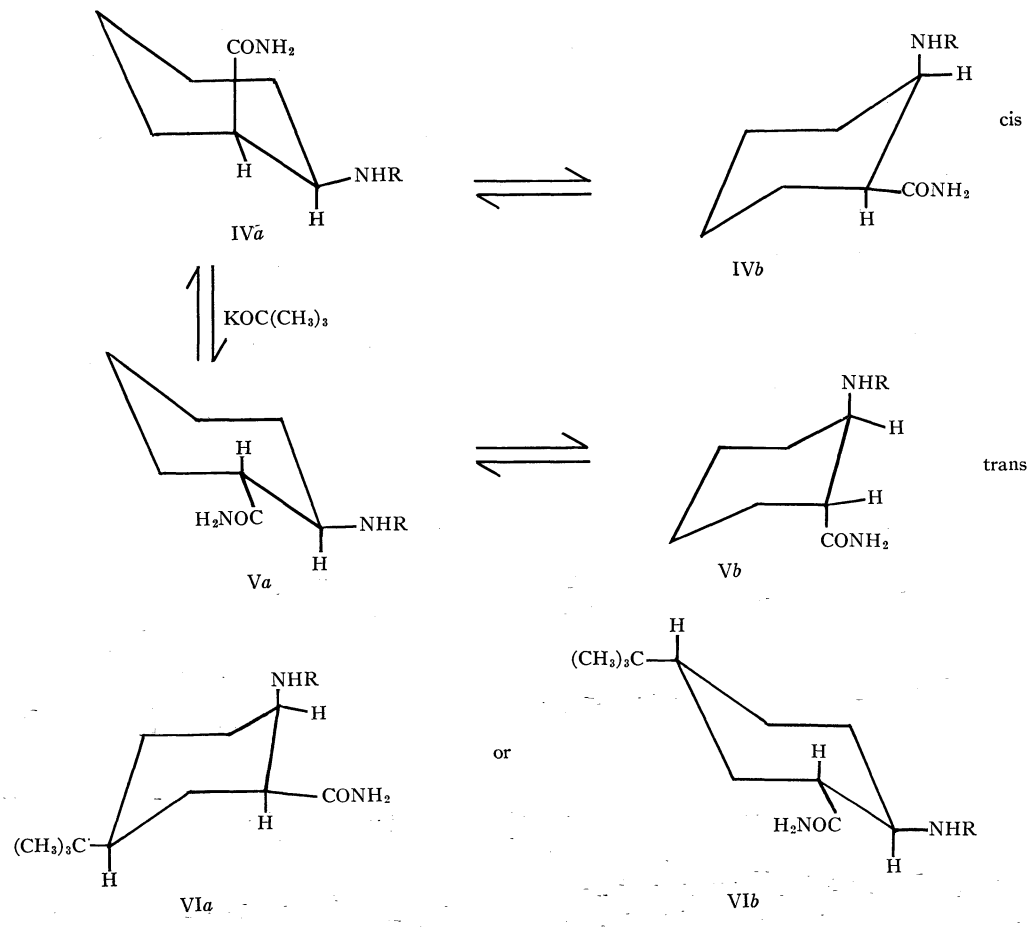


III

of producing *sym*-octahydroacridine involves condensation with ammonia and then oxidative aromatization.

The previous assignment (1) of a cis configuration to cyclohexyl 2-carbamylcyclohexylamine (IV*a* $\rightleftharpoons$ IV*b*) was confirmed by its equilibration in the presence of potassium tertiary butoxide. The equilibration product containing the trans epimer (V*a* $\rightleftharpoons$ V*b*) melted at 95° and on nitrosation gave a nitrosamine melting at 158°. The nitrosamine from the cis epimer (IV*a* $\rightleftharpoons$ IV*b*) melted at 167°. Infrared spectra of the epimeric cyclohexyl 2-carbamylcyclohexylamines and their N-nitroso derivatives also show distinct differences (see Table II).

Several attempts to equilibrate 4-*t*-butylcyclohexyl 2-carbamyl-4-*t*-butylcyclohexylamine were unsuccessful. The original compound was recovered in good yields in each experiment. Thus 4-*t*-butylcyclohexyl 2-carbamyl-4-*t*-butylcyclohexylamine must possess conformation VI*a* (cis 1*a*, 2*e*/cis 2*e*, 4*e*) or VI*b* (trans 1*e*, 2*e*/cis 2*e*, 4*e*). This conformation VI*a* would be formed by cis addition of hydrogen at the less hindered approach to the double bond. This conformation with the carbamyl group equatorial is stabilized by the 4-*t*-butyl group which prevents the ring from flipping over into the conformation with the carbamyl group axial and the amino substituent equatorial. Conformation VI*b* with all substituents equatorial could account also for the stability of the 4-*t*-butyl compound. Formation of conformation VI*b* can be explained by the migration of a double bond prior to hydrogenation. Actually the hydrogenation of cyclohexylidene 2-carbamylcyclohex-1-enylamine proceeded at a much more rapid rate than the hydrogenation of its 4-*t*-butyl derivative. The former compound absorbed two mole equivalents of hydrogen in 2 hours while 4-*t*-butylcyclohexylidene 2-carbamyl-4-*t*-butylcyclohex-1-enylamine absorbed one mole equivalent of hydrogen in 1 hour and then required an additional 20 hours to absorb a further 0.6 mole equivalents.



R = cyclohexyl or 4-*t*-butylcyclohexyl.

Cyclopentyl 2-carboxylcyclopentylamine was prepared by hydrolysis of the hydrogenation product from cyclopentylidene 2-carbamylcyclopent-1-enylamine. Attempts to prepare cyclopentyl 2-carboxylcyclopentylamine by other routes were unsuccessful. After heating cyanocyclopent-1-ene and cyclopentylamine in glacial acetic acid at 113° for 19 hours, the reagents were recovered unchanged. Heating an aqueous solution of cyclopentylamine and cyclopent-1-enylcarboxylic acid in a sealed tube at 155° for 48 hours gave mainly N-cyclopentyl cyclopent-1-enylcarboxamide (m.p. 141.5°).

EXPERIMENTAL*

4-t-Butylcyclohexanone

4-*t*-Butylcyclohexanone (m.p. 42°) was prepared in 75% yield from 4-*t*-butylcyclohexanol by the procedure described (6) for the conversion of menthol to menthone. The product was purified by distillation at 95–97° at 3 mm; m.p. 47°; oxime m.p. 137° (lit. (7) 137.5–138.5°).

Reaction of Alicyclic Ketones with Urea and Thiourea

The compounds listed in Table I were prepared by one of the following procedures.

**All melting points are uncorrected. Microanalyses were determined by Dr. C. Daessle, Montreal, Quebec.*

Method A.—Cyclohexanone (19.6 g, 0.2 mole) and urea (24 g, 0.4 mole) in *o*-xylene (20 ml) were heated at reflux for 40 minutes. Water was distilled azeotropically and it was collected in a Barrat trap. The reaction was cooled and water (50 ml) and benzene (25 ml) were added. The precipitate (m.p. 199–205°) was recovered by filtration, yield 19.9 g (90%). Recrystallization from 46% aqueous ethanol (175 ml) gave pure cyclohexylidene 2-carbamylcyclohex-1-enylamine (m.p. 224–225°), yield 13.8 g. A mixed melting point determination with a known sample gave no depression.

Method B.—Cyclohexanone (19.6 g, 0.2 mole) and urea (24 g, 0.4 mole) in a solution of *o*-xylene (20 ml) and dimethylformamide (75 ml) were heated under reflux for 2.6 hours. During the reaction period water was collected azeotropically in a Barrat trap. The solution was evaporated *in vacuo* to one-half of its original volume and the residual solution was diluted with water (150 ml). The product (m.p. 215°) was collected by filtration, yield 18.5 g (84%). Recrystallization from 45% aqueous ethanol (270 ml) gave pure product (m.p. 225–226°), yield 15.2 g. A mixed melting point determination with a sample of product from method A showed no depression.

Cyclohexyl 2-Carbamylcyclohexylamine Hydrochloride and Free Base

The hydrochloride (m.p. 276°) and free base (m.p. 128°) of this compound were prepared as previously described (1).

Cyclohexyl 2-Carbamylcyclohexylnitrosamine

Cyclohexyl 2-carbamylcyclohexylamine hydrochloride (0.4 g, 0.0015 mole) in aqueous hydrochloric acid (5 drops of concentrated hydrochloric acid in 25 ml water) was treated with an aqueous solution of sodium nitrite (1 g sodium nitrite in 5 ml water). This solution was allowed to stand at room temperature for 24 hours. Crystals (m.p. 162–165°) gradually separated from the solution, yield 0.14 g (36%). One recrystallization from aqueous ethanol raised the melting point to 165–167°. Anal. Calc. for $C_{13}H_{23}N_3O_2$: C, 61.63; H, 9.15; N, 16.59. Found: C, 61.44; H, 9.00; N, 16.55.

Equilibration of Cyclohexyl 2-Carbamylcyclohexylamine

Cyclohexyl 2-carbamylcyclohexylamine (1 g, 0.004 mole) in 20 moles of potassium *t*-butoxide solution (1.3 g of metallic potassium in 33 ml *t*-butanol) was heated under reflux for 1 hour. At the end of the reaction period the solution was diluted with 7 volumes of water and exhaustively extracted with chloroform. Evaporation of the chloroform extract *in vacuo* gave an oil which crystallized into needle-like crystals (m.p. 94–95°) on standing, yield 1 g (100%). Several recrystallizations of the product from ethyl acetate gave crystals with melting ranges varying between 75° and 90°. Anal. Calc. for $C_{13}H_{24}N_2O$: C, 69.60; H, 10.78; N, 12.49. Found: C, 69.45; H, 11.00; N, 12.21. This experiment was repeated several times with the same results.

Nitrosation of Equilibration Product from Cyclohexyl 2-Carbamylcyclohexylamine

To a solution of this equilibration product (1.9 g, 0.008 mole) in water (40 ml) containing concentrated hydrochloric acid (1.7 g, 0.017 mole) was added a solution of sodium nitrite (1.25 g, 0.017 mole) in water. After standing overnight at room temperature crystals (m.p. 156–158°) of the nitrosamine separated, yield 0.71 g (33%). Two recrystallizations from aqueous ethanol raised the melting point to a constant value of 158°. Anal. Calc. for $C_{13}H_{23}N_3O_2$: C, 61.63; H, 9.15; N, 16.59. Found: C, 61.61; H, 9.33; N, 16.94. The melting point of this epimeric nitrosamine was depressed on admixture with a sample of the nitrosamine (m.p. 167°) which was prepared from cyclohexyl 2-carbamylcyclohexylamine melting at 128° (*vide supra*).

4-t-Butylcyclohexyl 2-Carbamyl-4-t-butylcyclohexylamine

A solution of 4-*t*-butylcyclohexylidene 2-carbamyl-4-*t*-butylcyclohex-1-enylamine (2 g, 0.006 mole) in absolute ethanol (150 ml) containing concentrated hydrochloric acid (0.6 g) and platinum oxide (0.1 g) catalyst was hydrogenated at room temperature. The first mole equivalent of hydrogen was absorbed very rapidly and then hydrogenation proceeded very slowly. After 20.5 hours only 1.6 mole equivalent of hydrogen was absorbed. The reaction mixture was filtered and the filtrate was evaporated to dryness *in vacuo*. The amorphous residue was dissolved in water and the solution made alkaline with 5% aqueous sodium hydroxide solution. A white precipitate separated from solution. This mixture was extracted with chloroform and the chloroform extract was evaporated to dryness *in vacuo*. The residue (m.p. 189°) weighed 0.8 g (41% yield). Four recrystallizations from ethyl acetate raised the melting point to 194°. Anal. Calc. for $C_{21}H_{40}N_2O$: C, 74.94; H, 11.98; N, 8.33. Found: C, 75.04; H, 12.02; N, 8.10.

Attempt to Epimerize 4-t-Butylcyclohexyl 2-Carbamyl-4-t-butylcyclohexylamine

Several attempts to epimerize 4-*t*-butylcyclohexyl 2-carbamyl-4-*t*-butylcyclohexylamine (m.p. 194°) under the conditions employed for the equilibration of cyclohexyl 2-carbamylcyclohexylamine gave almost quantitative recoveries of unchanged starting material.

4-Methylcyclohexyl 2-Carbamyl-4-methylcyclohexylamine Hydrochloride

4-Methylcyclohexylidene 2-carbamyl-4-methylcyclohex-1-enylamine (6 g, 0.024 mole) in absolute ethanol (250 ml) containing concentrated hydrochloric acid (2.04 ml) and 109 mg of platinum oxide was hydrogenated at ambient temperature and pressure. Approximately two mole equivalents of hydrogen were absorbed in 35 minutes. The catalyst was removed by filtration and the filtrate was evaporated to a volume

of 25 ml *in vacuo*. After the residual solution was treated with ether (75 ml) and a few drops of concentrated hydrochloric acid, a crystalline precipitate (m.p. 216–217°) was obtained, yield 4.9 g (70%). A sample (1 g) was purified by several crystallizations from ethanol–ether solution, yield 0.41 g. The final melting point was 223–224°. Anal. Calc. for $C_{15}H_{29}ClN_2O$: C, 62.36; H, 10.12; Cl, 12.28; N, 9.70. Found: C, 62.00; H, 10.04; Cl, 12.68; N, 9.61.

A portion (1 g, 0.003 mole) of this hydrochloride salt in 15 ml of water was treated with excess aqueous sodium hydroxide solution. The resulting alkaline mixture was extracted with chloroform and the chloroform extract was dried over anhydrous sodium sulphate. Evaporation of chloroform solution gave 0.8 g (93%) of solid (m.p. 108–109°). One recrystallization from ether–pentane solution raised the melting point of 4-methylcyclohexyl 2-carbamyl-4-methylcyclohexylamine to 114–115°. Anal. Calc. for $C_{15}H_{28}N_2O$: C, 71.37; H, 11.18; N, 11.10. Found: C, 71.51; H, 11.00; N, 11.47.

Cyclopentyl 2-Carbamylcyclopentylamine Hydrochloride

Cyclopentyl 2-carbamylcyclopentylamine hydrochloride (m.p. 210–211°) was prepared in 61% yield by the hydrogenation of cyclopentylidene 2-carbamylcyclopent-1-enylamine under the conditions described for the preparation of 4-methylcyclohexyl 2-carbamyl-4-methylcyclohexylamine hydrochloride. Two recrystallizations from ethanol–ether solution raised the melting point to 223–224°. Anal. Calc. for $C_{11}H_{21}ClN_2O$: C, 56.76; H, 9.09; Cl, 15.24; N, 12.04. Found: C, 57.02; H, 9.02; Cl, 15.23; N, 12.04.

Cyclopentyl 2-Carboxylcyclopentylamine Hydrochloride

A solution of cyclopentyl 2-carbamylcyclopentylamine hydrochloride (0.2 g, 0.001 mole) in concentrated hydrochloric acid (5 ml) was heated on a steam bath for 1 hour. The solution was evaporated to dryness *in vacuo* and the residue was dissolved in methanol (6 ml). On addition of ether (15 ml) to the methanolic solution a precipitate (40 mg) of ammonium chloride was obtained. The filtrate was evaporated to dryness and the residual oil readily crystallized (m.p. 165–170°), yield 0.2 g (99.6%). One recrystallization from methanol–ether solution raised the melting point to 180.5–181°. Anal. Calc. for $C_{11}H_{20}ClNO_2$: C, 56.52; H, 8.63; Cl, 15.17; N, 5.99. Found: C, 56.55; H, 8.57; Cl, 15.33; N, 6.25.

Cyanocyclopent-1-ene

Cyanocyclopent-1-ene (b.p. 70° at 20 mm, n_D^{23} 1.46978) was prepared in 62% yield by the method of Wheeler and Lerner (8).

Cyclopent-1-enecarboxylic Acid

Cyanocyclopent-1-ene was converted in 63% yield into cyclopent-1-enecarboxylic acid (m.p. 121–122°; lit. (8) 121°) by the procedure of Wheeler and Lerner (8).

Cyclopentylamine

A solution of cyclopentanone (67.2 g, 0.8 mole) and hydroxylamine hydrochloride (69.5 g, 1 mole) in water (120 ml) was treated with an aqueous solution of sodium carbonate (53 g sodium carbonate in 130 ml water). After stirring for 30 minutes, the crystalline cyclopentanone oxime (m.p. 56.5–57.5°)was recovered by filtration, yield 53 g (67%).

The oxime (30 g, 0.3 mole) in absolute ethanol (700 ml) was treated with small portions of sodium metal (100 g). This mixture was refluxed for 12 hours until all the sodium disappeared. The viscous syrup was treated with an equal volume of water and the solution was exhaustively extracted with ether. After the ether extract was acidified with dry hydrogen chloride, it was evaporated to dryness. The residue was treated with 15% aqueous sodium hydroxide solution and this solution was extracted with ether. The ether was removed by fractional distillation through a Widmer column and the residual amine was fractionated in a spinning band column. Cyclopentylamine (b.p. 106–108°, n_D^{25} 1.44691; lit. (9) b.p. 106–108°, n_D^{25} 1.4478) was obtained in 47% yield.

Attempts to Prepare Cyclopentyl 2-Cyanocyclopentylamine

A solution of cyanocyclopent-1-ene (0.94 g, 0.001 mole) and cyclopentylamine (0.86 g, 0.001 mole) in glacial acetic acid (3 ml) was heated at 113° for 19 hours. The dark solution was made alkaline with 15% aqueous sodium hydroxide solution (20 ml) and extracted with ether. Washing the ether phase with 10% hydrochloric acid gave 1.12 g (91%) of cyclopentylamine hydrochloride (m.p. 200–202°).

The ether phase was washed with aqueous sodium bicarbonate solution and water and dried over anhydrous sodium sulphate. Evaporation of the ether solution gave 0.88 g (94%) of unchanged cyanocyclopent-1-ene.

The results were the same after the above reagents were heated for 22 hours at 113°.

Attempt to Prepare Cyclopentyl 2-Carboxycyclopentylamine

A solution of cyclopentylamine (2.34 g, 0.027 mole) and cyclopent-1-enylcarboxylic acid (1 g, 0.009 mole) in water (5 ml) was heated in a sealed tube at 155° for 48 hours. The resulting mixture was extracted with ether and the ether extract was washed with 10% hydrochloric acid and water. The ether extract on evaporation gave a solid which melted at 80–95°, yield 0.6 g (37%). Two recrystallizations from aqueous ethanol raised the melting point to 141–141.5°. This compound was identified as N-cyclopentyl cyclopent-1-enylcarboxamide by analysis and its infrared spectrum. Anal. Calc. for $C_{11}H_{17}NO$: C, 73.69; H, 9.56. Found:

C, 73.48; H, 9.47. Infrared spectrum of the solid in Nujol mull showed absorption bands at 1328, 1604, 1620, 1641, and 3330 cm^{-1}.

A mixture of oil and cyclopentylamine hydrochloride was obtained from the acidic aqueous washings of the ether extract. The crystals (m.p. 199–200°) were identified as cyclopentylamine hydrochloride by a mixed melting point determination, yield 0.4 g. Attempts to purify the remaining dark brown oil were unsuccessful. It did not have the properties expected for cyclopentyl 2-carboxycyclopentylamine.

2,2′-Methylene-bis-cyclohexanone

A modification of the procedure described by Wick and Becke (10) was used for the preparation of 2,2′-methylene-bis-cyclohexanone.

Cyclohexanone (98 g, 1 mole), dimethylamine hydrochloride (18 g, 0.2 mole), and 30% formalin (20 g, 0.2 mole) were mixed and heated gradually on an oil bath. An exothermic reaction occurred at a bath temperature of 120° and the reaction was allowed to proceed without further heating. After the reaction had subsided, the product was cooled to room temperature and 20% aqueous sodium hydroxide solution (45 g) was added. After thorough agitation, the organic layer was separated and the water and unreacted cyclohexanone were removed by distillation. When the distillation temperature reached 155°, the residue was refluxed until the reflux temperature reached 162° after which the residue was distilled *in vacuo*. The main fraction (b.p. 168–170° at 5 mm, yield 38.3 g) was refractionated in a spinning band column. The first fraction (b.p. 120° at 0.05 mm, yield 9.7 g) remained an oil while the second fraction (b.p. 104° at 0.02 mm) crystallized (m.p. 52°; lit. (11) 58°), yield 15 g (36%). Anal. Calc. for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 74.34; H, 9.39.

1,2,3,4,5,6,7,8-Octahydroacridine

A solution of 2,2′-methylene-bis-cyclohexanone (2 g, 0.02 mole) and urea (2 g, 0.03 mole) in dimethylformamide (15 ml) – xylene (5 ml) solution was heated under reflux until no more water separated in the Barrat trap. The reaction mixture was diluted with water and extracted with chloroform. The chloroform extract was evaporated to dryness and the residual oil was dissolved in methanol, diluted with an equal volume of water, and acidified with concentrated hydrochloric acid. The solution was extracted with ether and the aqueous phase was made alkaline with aqueous sodium hydroxide solution. The alkaline solution was exhaustively extracted with chloroform and the chloroform extract was evaporated *in vacuo*. The residual oil was dissolved in a small amount of ethyl acetate and the solution was filtered. Evaporation of the filtrate to dryness gave an oil which crystallized at room temperature, yield 1.75 g (97%). This crude product melted at 50°. It was dissolved in benzene and the benzene solution was passed through a column of neutral alumina. Evaporation of the benzene eluate *in vacuo* gave 1.2 g of crystals melting at 65–68°. These crystals were sublimed *in vacuo* and the sublimate melted at 69–71° (lit. (4, 5) 69° and 73.4–74°). Anal. Calc. for $C_{13}H_{17}N$: C, 83.37; H, 9.15; N, 7.48. Found: C, 83.65; H, 9.01; N, 7.19.

Ultraviolet absorption spectrum in ethanol gave λ_{max} 216, 222, 272, 276.5, 281, 285, and 290 mμ with $\epsilon_{max} \times 10^{-3}$ 6.3, 4.5, 4.3, 6.5, 7.8, 7.1, and 5.6 respectively.

A picrate (m.p. 195°) was prepared in 94% yield in the usual manner from a methanolic solution of the free base. Two crystallizations from ethanol raised the melting point to 200° with dec. (lit. (5) m.p. 200–201.5°). Anal. Calc. for $C_{19}H_{20}N_4O_7$: C, 54.80; H, 4.84; N, 13.46. Found: C, 54.96; H, 4.96; N, 13.31.

The hydrochloride (m.p. 201–202°) was prepared in 98% yield by passing dry hydrogen chloride through an ether solution of the free base. Anal. Calc. for $C_{13}H_{18}ClN$: C, 69.79; H, 8.10; Cl, 15.85; N, 6.26. Found: C, 69.83; H, 7.46; Cl, 15.79; N, 6.31.

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