Reaction of 3,5,5-trimethylpyrazoline with perbenzoic acid. To a solution of 75 ml. of 1.05*M* perbenzoic acid[26] in methylene chloride was added 5.6 g. (0.05 mole) of 3,5,5-trimethylpyrazoline[25] in 50 ml. of methylene chloride at −5–0° during a 45-min. period. The mixture was stirred at 5–15° overnight, made basic by the addition of solid sodium carbonate, and diluted with water. The organic layer was separated, combined with methylene chloride extracts of the aqueous layer, dried, and concentrated. A yellow oil that crystallized upon standing was obtained; yield 1.8 g. (14%). Recrystallization from hexane yielded white platelets, m.p. 88–89°.

Anal. Calcd. for $C_{13}H_{16}N_2O_3$: C, 62.88; H, 6.50; N, 11.28. Found: C, 63.05; H, 6.70; N, 10.88.

Its infrared spectrum showed bands attributable to an aromatic ester (1725 cm.$^{-1}$) and an azoxy group (1520 cm.$^{-1}$). Its NMR spectrum (Table I) indicated the presence of three methyl groups; quartet at 7.60, 7.28, 7.00, and 6.65 τ is due to two slightly nonequivalent protons.[27] Treatment of this material with potassium hydroxide in ethanol at 20° for 15 min. converted it to 3,5,5-trimethylisopyrazole 1-oxide. All these features are nicely accommodated by structure VIII.

Dibromopernitrosomesityl oxide (V). This material was prepared by the published method.[9b] Its ultraviolet spectrum in ethanol showed a maximum at 290 mμ, ϵ_{max} 7000 and a broader band centering at λ_{max} 233, ϵ_{max} 2500. The longer wave length band is consistent with the structure V as nitroso dimers absorb in this region.[18]

4-Bromo-3,5,5-trimethylisopyrazole 1,2-dioxide.[9b] The ultraviolet spectrum of this material showed maxima at λ_{max} 327, ϵ_{max} 3700, λ_{max} 220, ϵ_{max} 8300. Its infrared spectrum was also similar in the 6–7 μ region to that of Ic.

Preparation of 3,5,5-trimethyl-4-isoxazolone oxime. A solution of 7.1 g. (0.05 mole) of pernitrosomesityl oxide in 25 ml. of acetonitrile was heated under reflux for 5 hr. Nitrogen oxides were evolved. Upon removal of the solvent a solid residue was obtained which was recrystallized from hexane–chloroform, m.p. 156–157° (lit.[2,4] m.p. 156°). Its infrared spectrum showed hydroxyl absorption at 3 μ and C=N absorption at 1655 cm.$^{-1}$. Its NMR spectrum (measured in CH_2Cl_2) showed singlets at 8.05 τ [$(CH_3)_2C$], 7.65 τ (CH_3C=N), and 0.88 τ (=N—OH).

HUNTSVILLE, ALA.

(26) L. S. Silbert, E. Siegel, and D. Swern, Abstracts, 139th Meeting of the American Chemical Society, St. Louis, Mo., April 1961, p. 15-O.

(27) Ref. 14, p. 85.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

Heterocyclic Compounds. X. Hydrogenated Derivatives of Isoindole and 2-Azaazulene from Reductive Cyclization of γ-Nitro Ketones[1]

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Received September 29, 1961

Nitromethane, nitroethane, and 2-nitropropane condensed with α,β-unsaturated cycloalkenyl ketones to yield a series of γ-nitro ketones (see Table I).

Hydrogenation of representative nitro ketones over Raney nickel yielded Δ^1-pyrrolines (XIII and XIX). Hydrogenation of the nitro ketones over platinum yielded mixtures of the corresponding pyrrolidines (XVa and XVIIa) and cyclic hydroxylamines (XVI and XVIII).

When pyrrolines XIII and XIX were hydrogenated over platinum, pyrrolidines XVb and XVIIb, isomeric with XVa and XVIIa, were obtained. Evidently pyrrolines are not the precursors of pyrrolidines in reductive cyclization of these γ-nitro ketones. Hydroxylamine XVI is not the intermediate in reductive cyclization of nitro ketone VII to pyrrolidine XVa over platinum, nor does this reaction proceed by initial reduction of the keto group.

Earlier papers in this series, and others cited therein, suggest that reductive cyclization of γ-nitro ketones is a potentially versatile method for synthesis of hydrogenated and partially hydrogenated nitrogen heterocycles. Our investigations now have been extended to a series of γ-nitro ketones containing a five-, six-, or seven-membered ring, reduction of which might be expected to yield fused ring systems.

Representative γ-nitro ketones were prepared by Michael type condensations of nitro alkanes with α,β-unsaturated cycloalkenyl ketones (see Table I). Nitromethane, nitroethane, and 2-nitropropane reacted with 1-acetylcyclopentene to give comparable yields of the respective γ-nitro ketones. With 1-acetylcyclohexene and 1-acetylcycloheptene, yields of nitro ketones varied considerably, evidently because of steric factors dependent upon size of ring and complexity of nitro alkane. In the presence of sodium ethoxide, 2-nitropropane gave no adduct with 1-acetylcyclohexene, even after two days in boiling ethanol.

Low pressure hydrogenation of 1-acetyl-2-nitromethylcyclohexane (VII) and 1-acetyl-2-nitromethylcycloheptane (X) over Raney nickel yielded pyrroline derivatives XIII and XIX, respectively. These pyrrolines exhibit the spectral and chemical properties characteristic of other Δ^1-pyrrolines.[2-5] They show strong imine absorption in the 6.1-μ

(1) Abstracted from a portion of the Ph.D. dissertation of Satinder Kessar.

(2) M. C. Kloetzel, J. L. Pinkus, and R. M. Washburn, *J. Am. Chem. Soc.*, 79, 4222 (1957).

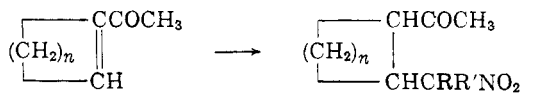
(3) M. C. Kloetzel and J. L. Pinkus, *J. Am. Chem. Soc.*, 80, 2332 (1958).

(4) M. C. Kloetzel, F. L. Chubb, and J. L. Pinkus, *J. Am. Chem. Soc.*, 80, 5773 (1958).

(5) M. C. Kloetzel, F. L. Chubb, R. Gobran, and J. L. Pinkus, *J. Am. Chem. Soc.*, 83, 1128 (1961).

TABLE I

CONDENSATION OF NITRO ALKANES WITH CYCLOALKENYL KETONES



I, $n = 3$; II, $n = 4$; III, $n = 5$ IV-XII

Nitro Ketone	Reaction Period, Days[a]	Yield, %
IV, $n = 3$; R = R¹ = H	20	69
V, $n = 3$; R = H; R¹ = CH_3	20	68
VI, $n = 3$; R = R¹ = CH_3	20	66
VII, $n = 4$; R = R¹ = H	20	56
VIII, $n = 4$; R = H; R¹ = CH_3	20	12
IX, $n = 4$; R = R¹ = CH_3	40	0
X, $n = 5$; R = R¹ = H	5	63
XI, $n = 5$; R = H; R¹ = CH_3	5	39
XII, $n = 5$; R = R¹ = CH_3	20	15

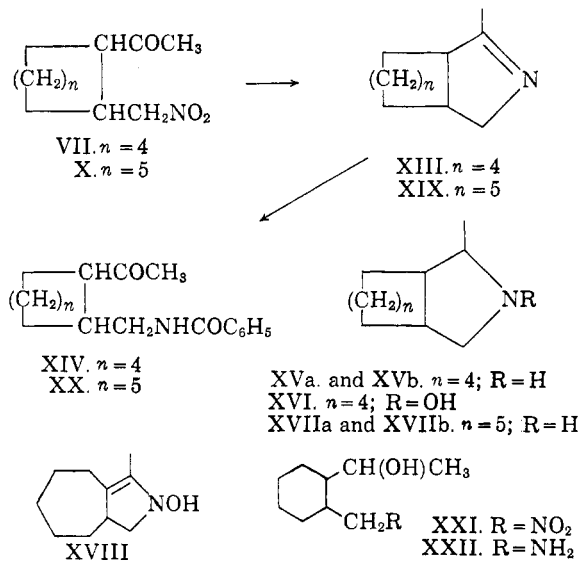
[a] Reaction conducted at room temperature in ethanol, employing 0.16 mole cycloalkenyl ketone, 0.16 mole sodium ethoxide, and 1.6 moles nitro alkane.

region[6] and undergo benzoylation with concomitant hydrolytic cleavage of the pyrroline ring to yield keto amides XIV and XX.

Low pressure hydrogenation of 1-acetyl-2-nitromethylcyclohexane (VII) over platinum afforded a 48% yield of the pyrrolidine XVa, together with 29% of the saturated hydroxylamine XVI. Compound XVa gave a Hinsberg test characteristic of a secondary amine, produced a phenylthiourea derivative, and showed absorption at 3 μ but not in the 6-μ region. Similarly, XVI absorbed in the 3-μ region but not in the 6 μ region; this compound, however, gave a positive Tollens test.

Hydrogenation of 1-acetyl-2-nitromethylcycloheptane (X) over platinum also yielded the corresponding pyrrolidine (XVIIa), accompanied in this instance by a substance that appeared to be an unsaturated hydroxylamine. Because this substance showed medium absorption at 2.94 μ and strong absorption at 6.21 μ and also gave a positive Tollens test, it has been assigned tentatively the structure XVIII, rather than that of the isomeric nitrone.[7]

The isolation of partially reduced products such as XIII, XVI, XVIII, and XIX raises a question concerning the sequence of events by which nitro ketones VII and X are reduced to the respective pyrrolidines XVa and XVIIa. It is of interest that no pyrroline XIII could be isolated when the hydrogenation of VII over platinum was interrupted before reaction was complete. While in no way conclusive, this experiment suggests that XIII is not an intermediate in the platinum-catalyzed reductive cyclization of VII to XVa. That XIII was indeed not the intermediate was confirmed when the platinum-catalyzed reduction of XIII was found to yield a stereoisomeric pyrrolidine, XVb, whose picrate melted at 162–163° and phenylthiourea at 167–168°, rather than pyrrolidine XVa, whose picrate melted at 134.5–135.5° and phenylthiourea at 127–127.5°. Reduction of XIII with lithium aluminum hydride also yielded XVb.



Similarly, a platinum-catalyzed hydrogenation of XIX yielded a stereoisomeric pyrrolidine, XVIIb, whose picrate melted at 167–168° and benzenesulfonamide at 102–103°, rather than pyrrolidine XVIIa, whose picrate melted at 173–175° and benzenesulfonamide at 91.5–92°.

Hydroxylamine XVI also can be eliminated as a a precursor of XVa, as XVI is not easily reduced. Prolonged subjection of VII to hydrogenation conditions over platinum failed to alter materially the yields of XVa and XVI obtained.

1-Acetyl-2-nitromethylcyclohexane (VII) was reduced selectively with sodium borohydride to yield 1 - (1 - hydroxyethyl) - 2 - nitromethylcyclohexane (XXI). Further hydrogenation of XXI, under conditions formerly used to convert VII to XVa, yielded amino alcohol XXII. It is evident, therefore, that conversion of VII to XVa does not proceed by initial reduction of the keto group.

EXPERIMENTAL[8]

γ-Nitro ketones. In Table I are listed the nitro ketones that were prepared by the following typical procedure.

(6) As commonly prepared, these pyrrolines show weak absorption in the 3-μ region. This absorption is diminished considerably when the bases are dried over potassium hydroxide and is attributed to moisture which is difficult to remove.

(7) Compare ref. 5.

(8) Melting points are uncorrected. Microanalyses are by Dr. Adalbert Elek, Elek Microanalytical Laboratories, Los Angeles, Calif.; by Micro-Tech Laboratories, Skokie, Ill.; and by William J. Schenck, formerly of the University of Southern California. Infrared spectra were determined with a Perkin-Elmer Model 13 double beam spectrophotometer equipped with sodium chloride prism.

Freshly distilled nitromethane (100 g.) was added to a mixture of 1-acetylcyclohexene[9] (20 g.) and the sodium ethoxide solution prepared from sodium (3.70 g.) and ethanol (300 ml.). After being allowed to stand for 20 days at room temperature, the mixture was acidified with glacial acetic acid and was then concentrated to a thick slurry by evaporation on a steam bath. An ethereal extract of the slurry was washed with water, dried over sodium sulfate, and fractionated through a 70-cm. Podbielniak column. *1-Acetyl-2-nitromethylcyclohexane* (VII, 16.6 g.) distilled at 105–107° at 1.5 mm. pressure.

Anal. Calcd. for $C_9H_{15}NO_3$: C, 58.35; H, 8.16; N, 7.56. Found: C, 58.17; H, 8.17; N, 7.62.

The 2,4-dinitrophenylhydrazone was prepared by adding the nitro ketone to an equivalent quantity of 2,4-dinitrophenylhydrazine sulfate in 95% ethanol. Recrystallization from ethanol yielded orange needles, m.p. 126–128°.

Anal. Calcd. for $C_{15}H_{19}N_5O_6$: C, 49.31; H, 5.24; N, 19.17. Found: C, 49.58; H, 5.34; N, 19.33.

1-Acetyl-2-nitromethylcyclopentane (IV), prepared from 1-acetylcyclopentene,[10] distilled at 113–116° at 1.5 mm.

Anal. Calcd. for $C_8H_{13}NO_3$: C, 56.12; H, 7.65; N, 8.18. Found: C, 56.40; H, 7.74; N, 8.54.

The 2,4-dinitrophenylhydrazone separated from methanol in orange needles, m.p. 129–130°.

Anal. Calcd. for $C_{14}H_{17}N_5O_6$: C, 47.86; H, 4.87; N, 19.94. Found: C, 47.95; H, 5.00; N, 20.27.

1-Acetyl-2-(1-nitroethyl)cyclopentane (V) distilled at 91–92° at 1 mm.

Anal. Calcd. for $C_9H_{15}NO_3$: C, 58.35; H, 8.16; N, 7.56. Found: C, 58.37; H, 8.19; N, 7.77.

The 2,4-dinitrophenylhydrazone separated from methanol in orange needles, m.p. 111.5–113°.

Anal. Calcd. for $C_{15}H_{19}N_5O_6$: C, 49.31; H, 5.24; N, 19.17. Found: C, 49.25; H, 5.24; N, 19.38.

1-Acetyl-2-(1-methyl-1-nitroethyl)cyclopentane (VI) distilled at 91–92° at 1 mm.

Anal. Calcd. for $C_{10}H_{17}NO_3$: C, 60.29; H, 8.59; N, 7.03. Found: C, 59.67; H, 8.72; N, 7.14.

The 2,4-dinitrophenylhydrazone separated from methanol in orange needles, m.p. 123–124°.

Anal. Calcd. for $C_{16}H_{21}N_5O_6$: C, 50.64; H, 5.57; N, 18.46. Found: C, 50.65; H, 5.67; N, 18.61.

1-Acetyl-2-(1-nitroethyl)cyclohexane (VIII) distilled at 108–110° at 2 mm. The 2,4-dinitrophenylhydrazone separated from 95% ethanol in orange needles, m.p. 163.5–165°.

Anal. Calcd. for $C_{16}H_{21}N_5O_6$: C, 50.64; H, 5.57; N, 18.46. Found: C, 50.56; H, 5.60; N, 18.56.

1-Acetyl-2-nitromethylcycloheptane (X) distilled at 144–147° at 4 mm. as a yellow oil.

Anal. Calcd. for $C_{10}H_{17}NO_3$: C, 60.29; H, 8.59; N, 7.03. Found: C, 60.50; H, 8.50; N, 7.31.

The 2,4-dinitrophenylhydrazone separated from 95% ethanol in orange needles, m.p. 121–122°.

Anal. Calcd. for $C_{16}H_{21}N_5O_6$: C, 50.64; H, 5.57; N, 18.46. Found: C, 50.47; H, 5.65; N, 18.25.

The *1-acetylcycloheptene* (III) required for preparation of X was obtained by adding acetic anhydride (15.2 g.) dropwise to a stirred mixture of cycloheptene (16.4 g.) and anhydrous stannic chloride (40.0 g.) while the reaction mixture was maintained at 25–30°. An ether extract of the hydrolyzed (100 g. of crushed ice) reaction mixture was washed with sodium bicarbonate solution, dried, and fractionated. 1-Acetylcycloheptene (9.2 g., 44%) distilled at 94–97° at 17 mm.; $n^{23}D$, 1.4883. The 2,4-dintrophenylhydrazone of this product, m.p. 177–178°, did not depress the m.p. of an authentic sample.[10]

1-Acetyl-2-(1-nitroethyl)cycloheptane (XI) distilled at 122–124° at 4 mm.

Anal. Calcd. for $C_{11}H_{19}NO_3$: C, 61.93: H, 8.98; N, 6.57. Found: C, 61.79; H, 8.82; N, 6.54.

1-Acetyl-2-(1-methyl-1-nitroethyl)cycloheptane (XII) distilled at 154–155° at 4 mm. The 2,4-dinitrophenylhydrazone separated from 95% ethanol in orange needles, m.p. 143–144°.

Anal. Calcd. for $C_{18}H_{25}N_5O_6$: C, 53.07; H, 6.18; N, 17.19. Found: C, 53.12; H, 6.31; N, 16.78.

Hydrogenation of VII *over Raney Nickel.* A mixture of 10.5 g. of 1-acetyl-2-nitromethylcyclohexane (VII), 4.0 g. of Raney nickel, prepared[11] one week before use, and 130 ml. of 95% ethanol was subjected to hydrogenation at an initial pressure of 45 p.s.i. until absorption of hydrogen ceased (12 hr.). The filtered solution was evaporated in an atmosphere of nitrogen and finally under reduced pressure. Fractionation of the residue yielded 4.8 g. (62%) of *1-methyl-3a,4,5,6,7,7a-hexahydroisoindole* (XIII), b.p. 72–73° at 11 mm. pressure; $n^{18}D$, 1.4830. An infrared spectrum (liquid film) showed absorption maxima at 2.81 (vw), 3.33 (s), and 6.11 μ (s). The base slowly decolorized a neutral 1% solution of potassium permanganate.

Anal. Calcd. for $C_9H_{15}N$: C, 78.79; H, 11.03; N, 10.21. Found: C, 78.76; H, 11.02; N, 10.16.

The *picrate of* XIII separated from ethanol in yellow needles, m.p. 185–186°.

Anal. Calcd. for $C_{15}H_{18}N_4O_7$: C, 49.18; H, 4.95; N, 15.30. Found: C, 48.96; H, 5.14; N, 15.10.

A mixture of 800 mg. of XIII, 20 ml. of 10% aqueous sodium hydroxide, and 2 ml. of benzoyl chloride was shaken until excess benzoyl chloride was hydrolyzed. The semisolid product was extracted with ether and crystallized from petroleum ether (b.p. 40–50°) containing one drop of ethyl acetate; yield, 890 mg. of *1-acetyl-2-(benzoylaminomethyl)-cyclohexane* (XIV) in colorless needles from ethyl acetate, m.p. 140–141°. An infrared absorption spectrum (chloroform solution) of the amide showed maxima at 2.86 (m, N—H), 5.90 (s, ketonic carbonyl) and 6.07 μ (s, amido carbonyl).

Anal. Calcd. for $C_{16}H_{21}NO_2$: C, 74.08; H, 8.16; N, 5.40. Found: C, 74.09; H, 8.18; N, 5.31.

A mixture of 1.01 g. of XIII, 80 mg. of platinum oxide, and 60 ml. of 95% ethanol was subjected to hydrogenation for 20 hr. at an initial pressure of 46 p.s.i. The filtered solution was concentrated under nitrogen to a volume of 2 ml. (A drop of this solution gave no precipitated solid picrate when a drop of saturated ethanol solution of picric acid was added, indicating absence of starting XIII.)

Half of the concentrated solution was diluted with 10 ml. of anhydrous ether and a saturated ether solution of picric acid was added. The precipitated yellow *picrate of 1-methyl-octahydroisoindole* (XVb) (1.27 g.) separated from benzene in yellow needles, m.p. 162–163°.

Anal. Calcd. for $C_{15}H_{20}N_4O_7$: C, 48.90; H, 5.47; N, 15.21. Found: C, 48.76; H, 5.51; N, 15.33.

To the second half of the concentrated solution of XVb was added an equal volume of phenyl isothiocyanate. Trituration of the resulting product with a drop of 50% aqueous ethanol yielded a solid *phenylthiourea of* XVb that separated from 95% ethanol in colorless plates, m.p. 167–168°.

Anal. Calcd. for $C_{16}H_{22}N_2S$: C, 70.03; H, 8.07; N, 10.21. Found: C, 70.04; H, 8.14; N, 10.17.

A solution of 1.0 g. of XIII in 10 ml. of anhydrous ether was added dropwise to a stirred suspension of 1.5 g. of lithium aluminum hydride in 50 ml. of anhydrous ether. The mixture was stirred for 12 hr. at room temperature and excess hydride was destroyed by cautious addition of water. The filtered ether layer was then evaporated to a volume of 10 ml. and a saturated ether solution of picric acid was added. Precipitated picrate (1.31 g.) did not depress the m.p.

(9) E. E. Royals and C. M. Hendry, *J. Org. Chem.*, **15**, 1147 (1950).

(10) I. Heilbron, E. R. H. Jones, J. B. Toogood, and B. C. L. Weedon, *J. Chem. Soc.*, 1827 (1949).

(11) L. W. Covert and H. Adkins, *J. Am. Chem. Soc.*, **54**, 4116 (1932).

of the picrate of XVb obtained from hydrogenation of XIII over platinum.

Hydrogenation of VII *over platinum.* A mixture of 15 g. of 1-acetyl-2-nitromethylcyclohexane (VII), 300 mg. of platinum oxide, and 250 ml. of 95% ethanol was subjected to hydrogenation for 14 hr. at an initial pressure of 45 p.s.i. Fractionation of the products afforded 5.4 g. (48%) of *1-methyloctahydroisoindole* (XVa), b.p. 74–75° at 18 mm. pressure, and 3.63 g. (29%) of *2-hydroxy-1-methyloctahydroisoindole* (XVI), b.p. 113–114° at 8 mm. pressure.

When VII was subjected to the same hydrogenation conditions for 50 hr. the yields of XVa and XVI were 40% and 28%, respectively.

When hydrogenation of VII was conducted for only 40 min., the concentrated reaction mixture gave no precipitate when a saturated solution of picric acid in ethanol was added to it. By contrast, the same picric acid solution gave an immediate precipitate when added to a 4% solution of pyrroline XIII in ethanol.

An infrared absorption spectrum of XVa (liquid film) showed maxima at 3.00 (m), 3.36 (s), and 6.91 μ (s).

The *picrate of* XVa, prepared in ether solution, separated from benzene in yellow needles, m.p. 134.5–135.5°.

Anal. Calcd. for $C_{15}H_{20}N_4O_7$: C, 48.90; H, 5.47; N, 15.21. Found: C, 49.05; H, 5.42; N, 15.20.

The *phenylthiourea derivative of* XVa, crystallized from 95% ethanol, m.p. 127–127.5°. This m.p. was not changed when the material was recrystallized in the presence of a crystal of the phenylthiourea derivative of XVb.

Anal. Calcd. for $C_{16}H_{22}N_2S$: C, 70.03; H, 8.07; N, 10.21. Found: C, 69.86; H, 8.28; N, 10.07.

An infrared absorption spectrum of XVI (liquid film) showed maxima at 3.01 (m), 3.41 (s), and 6.90 μ (s). This material gave a positive Tollens test.

Anal. Calcd. for $C_9H_{17}NO$: C, 69.63; H, 11.04; N, 9.02. Found: C, 69.78; H, 11.01; N, 9.09.

Reduction of VII *with sodium borohydride.* A solution of 1.0 g. of sodium borohydride in 10 ml. of water was dropped slowly into a solution of 5.5 g. of 1-acetyl-2-nitromethylcyclohexane (VII) in 18 ml. of methanol. The *p*H of the reaction mixture was maintained between 3 and 7 by concurrent addition of 3 *N* sulfuric acid and the temperature of the reaction mixture was kept below 30° during the period of 60 min. required for the addition. After the solution had been made basic by addition of 25% aqueous sodium hydroxide, the organic product was extracted into ether and the ether extract was shaken repeatedly with saturated aqueous sodium bisulfite. Fractionation of the dried ether solution yielded 3.1 g. (56%) of *1-(1-hydroxyethyl)-2-nitromethylcyclohexane* (XXI), b.p. 130–132° at 3 mm. pressure; $n^{26}D$ 1.4856. Absence of ketonic function in this material was confirmed by absence of carbonyl absorption in its infrared spectrum and by the failure of the compound to give a 2,4-dinitrophenylhydrazone.

Anal. Calcd. for $C_9H_{17}NO_3$: C, 57.73; H, 9.15; N, 7.46. Found: C, 57.90; H, 9.06; N, 7.40.

A mixture of 3.0 g. of XXI, 60 mg. of platinum catalyst, and 50 ml. of 95% ethanol was subjected to hydrogenation at an initial pressure of 45 p.s.i. until absorption of hydrogen ceased. Fractionation of the filtered solution yielded 2.0 g. (80%) of *1-(1-hydroxyethyl)-2-aminomethylcyclohexane* (XXII), b.p. 110–115° at 3 mm. pressure; $n^{26}D$ 1.4916.

Anal. Calcd. for $C_9H_{19}NO$: C, 68.73; H, 12.17; N, 8.90. Found: C, 68.60; H, 12.20; N, 8.75.

Hydrogenation of X *over Raney nickel.* Hydrogenation of 1-acetyl-2-nitromethylcycloheptane (X) over Raney nickel, as described for VII, afforded a 59% yield of *1-methyl-3,3a,4,5,6,7,8,8a-octahydro-2-azaazulene* (XIX), b.p. 96–97° at 14 mm. pressure; $n^{21}D$, 1.4910. An infrared absorption spectrum of XIX (liquid film) showed maxima at 2.92 (vw), 3.42 (s), and 6.04 μ (s). The base slowly decolorized neutral 1% aqueous potassium permanganate.

The *picrate of* XIX separated from 95% ethanol in yellow needles, m.p. 147–148°.

Anal. Calcd. for $C_{16}H_{20}N_4O_7$: C, 50.52; H, 5.30; N, 14.73. Found: C, 50.69; H, 5.39; N, 14.63.

The *picrolonate of* XIX separated slowly when an anhydrous ether solution of the base was added to a saturated ethanol solution of an equivalent amount of picrolonic acid which had been diluted with five volumes of ether. The picrolonate separated from ethanol in brown needles, m.p. 167–168°.

Anal. Calcd. for $C_{20}H_{25}N_5O_5$: C, 57.82; H, 6.06; N, 16.85. Found: C, 57.85; H, 6.12; N, 17.15.

Pyrroline XIX reacted with benzoyl chloride, as described for XIII, to yield *1-acetyl-2-(benzoylaminomethyl)-cycloheptane* (XX); colorless needles from ethyl acetate, m.p. 97–98°. An infrared absorption spectrum of XX (chloroform solution) showed maxima at 2.90 (m), 5.90 (s), and 6.04 μ (s).

Anal. Calcd. for $C_{17}H_{23}NO_2$: C, 74.71; H, 8.48; N, 5.13 Found: C, 74.91; H, 8.60; N, 5.06.

When XIX was hydrogenated over platinum, as described for XIII, there was obtained *1-methyldecahydro-2-azaazulene* (XVIIb), which yielded almost quantitatively a picrate that separated from 95% ethanol in yellow needles, m.p. 167–168°.

Anal. Calcd. for $C_{16}H_{22}N_4O_7$: C, 50.24; H, 5.80; N, 14.66. Found: C, 50.41; H, 5.85; N, 14.74.

When shaken with benzenesulfonyl chloride and 5% aqueous sodium hydroxide, XVIIb yielded an alkali-insoluble benzenesulfonamide. Acidification of the filtrate gave no precipitate, confirming the absence of any primary amine. The *benzenesulfonamide of* XVIIb separated from ethyl acetate in colorless needles, m.p. 102–103°.

Anal. Calcd. for $C_{16}H_{23}NO_2S$: N, 4.77. Found: N, 4.69.

Hydrogenation of 1-acetyl-2-nitromethylcycloheptane (X) over platinum, as described for VII, yielded 32% of *1-methyldecahydro-2-azaazulene* (XVIIa), b.p. 84–87° at 5 mm. pressure, and 38% of *2-hydroxy-1-methyloctahydro-2-azaazulene* (XVIII) isolated as the picrate from the higher boiling residue.

Pyrrolidine XVIIa showed $n^{24}D$ 1.4912.

Anal. Calcd. for $C_{10}H_{19}N$: C, 78.36; H, 12.47; N, 9.14. Found: C, 78.22; H, 12.53; N, 9.23.

The *picrate of* XVIIa was prepared in dry ether and recrystallized from ethanol, m.p. 173–175°.

Anal. Calcd. for $C_{16}H_{22}N_4O_7$: C, 50.24; H, 5.80; N, 14.66. Found: C, 50.38; H, 5.86; N, 14.58.

The *benzenesulfonamide of* XVIIa, prepared as described for XVIIb, was crystallized from ethanol, m.p. 91.5–92°.

Anal. Calcd. for $C_{16}H_{23}NO_2S$: C, 65.48; H, 7.91; N, 4.77. Found: C, 65.67; H, 7.77; N, 4.80.

Hydroxylamine XVIII readily gave a positive Tollens test. An infrared absorption spectrum of XVIII (chloroform solution) showed maxima at 2.94 (m) and 6.21 μ (s).

The *picrate of* XVIII, prepared in dry ether, was crystallized from ethanol,m.p. 133–134°.

Anal. Calcd. for $C_{16}H_{20}N_4O_8$: C, 48.48; H, 5.10; N, 14.14. Found: C, 48.76; H, 5.12; N, 14.02.

Acknowledgment. The authors are indebted to Parke, Davis and Co., Detroit, Mich., for generous financial aid which made part of this study possible.

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