STUDIES IN THE PYRROLINE SERIES

V.[1] 3,3-DIMETHYL-1-PYRROLINE-1-OXIDE

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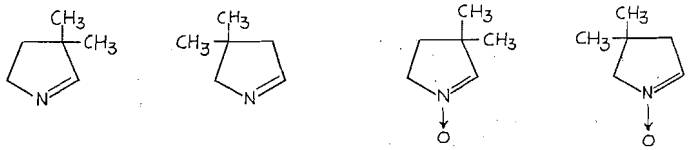
ABSTRACT

The pyrolysis of 1-ethyl-3,3-dimethylpyrrolidine-1-oxide gives 1-hydroxy-3,3-dimethylpyrrolidine, which, on dehydrogenation, yields 3,3-dimethyl-1-pyrroline-1-oxide. The identification of the nitrone is described. The cyclo-additions of styrene to this nitrone and to 5,5-dimethyl-1-pyrroline-1-oxide were investigated, and the direction of addition was deduced from the n.m.r. spectra of the adducts.

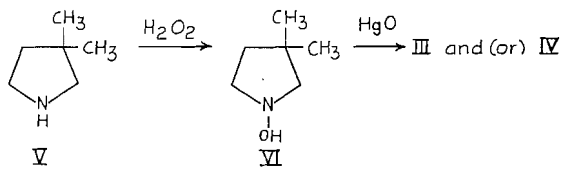
In connection with other work (1) it was desired to prepare pyrroline ring systems with geminal substitution at a β-position, and to this end attempts were made to synthesize one or more of the dimethyl compounds I–IV.



I II III IV

Three approaches were tried. The first followed the nitroalkane synthesis (2) and involved the attempted conjugate addition of nitromethane to senecialdehyde, this being the first step on the route to II and IV. Under a variety of reaction conditions, no absorption due to an unconjugated carbonyl group was found in the infrared spectrum of the product, and it was concluded that 1,4-addition had not occurred to an appreciable extent. This result is presumably due to the steric effect of the substituents at the β-position of the unsaturated aldehyde, and it is pertinent that, whereas nitromethane adds readily across the conjugated system of acrolein (3), in the reaction of crotonaldehyde with nitromethane, conjugate addition is not the main path.

The second approach, which suffered from the disadvantage that it would be expected to yield a mixture of isomers III and IV, was the direct oxidation of the corresponding secondary amine to the cyclic hydroxylamine (ref. 4, cf. 5) followed by dehydrogenation to the nitrone.



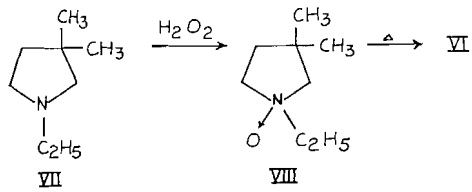
V VI

As others have recently reported (6, 7), some difficulty was experienced with the direct oxidation with hydrogen peroxide, a step which gave erratic and low yields. The best yield

[1]*For Part IV see R. Bonnett. J. Chem. Soc. 2313 (1965).*

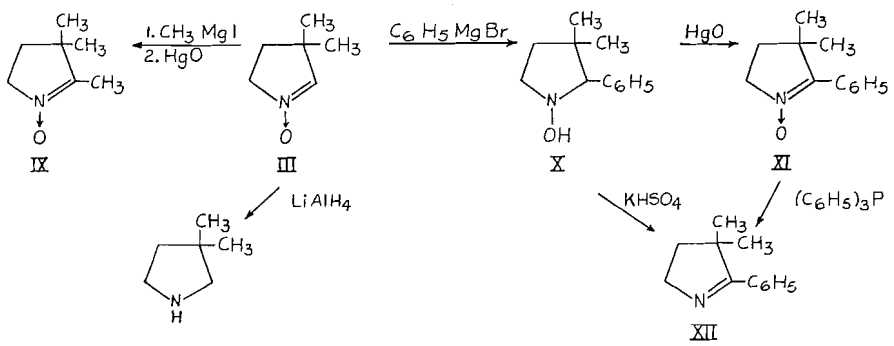
of solid 1-hydroxypyrrolidine (from pyrrolidine itself in preliminary experiments) was 8%; and from 3,3-dimethylpyrrolidine the corresponding hydroxylamine could not be isolated, although a trace of the nitrone (III) was obtained.

The third approach did prove successful as a preparative method. 1-Ethyl-3,3-dimethylpyrrolidine (VII) (from the corresponding imide) was converted into the amine oxide (VIII). This, on pyrolysis, eliminated 1-hydroxy-3,3-dimethylpyrrolidine (VI) (cf. ref. 7), which was characterized as the hydrogen oxalate. Oxidation of the cyclic hydroxylamine with yellow mercuric oxide in chloroform or dichloromethane yielded a hygroscopic oil, b.p. 74–76° at 0.55 mm, which solidified on cooling and which was identified as 3,3-dimethyl-1-pyrroline-1-oxide on the basis of the following evidence.



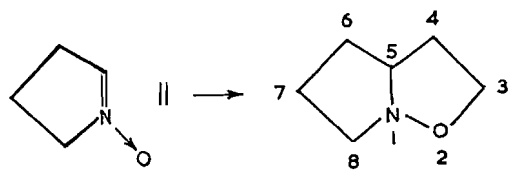
VII VIII

The product gave, not unexpectedly in view of its hygroscopic nature, rather poor analytical values itself, but these figures, and those for the picrate, indicated the molecular formula $C_6H_{11}NO$. Repeated fractionation of the picrate and its mother liquors did not furnish a second derivative. Reduction and hydrogenolysis of the product with lithium aluminium hydride/aluminium chloride gave 3,3-dimethyl pyrrolidine, which indicated that the ring system had remained intact. Both the infrared and ultraviolet spectra of the product were in accord with the nitrone formulation. In the infrared region a strong absorption at 1 580 cm^{-1} was assigned to the —CH=N → O system: 5,5-dimethyl-1-pyrroline-1-oxide shows a similar band at 1 573 cm^{-1} (8). The ultraviolet spectrum had λ_{max} 235 mμ (log ϵ 3.92) in ethanol and λ_{max} 248 mμ (log ϵ 3.98) in hexane. For comparison, 5,5-dimethyl-1-pyrroline-1-oxide has λ_{max} 234 mμ (log ϵ 3.89) in ethanol (8) and λ_{max} 247 mμ (log ϵ 3.94) in hexane. Ultraviolet irradiation produced a considerable decrease in absorption in all cases, presumably as a result of oxaziran formation (9). These results indicated that the base probably had structure III or IV, or could possibly be a mixture of the two. The double bond was located by a combination of chemical and physical methods. Reaction of the base with methyl magnesium iodide, followed by dehydrogenation of the product, furnished a trimethyl-1-pyrroline-1-oxide which (i) had the spectral characteristics of a ketonitrone rather than an aldonitrone (infrared band at ~1 610 cm^{-1} and not at ~1 580 cm^{-1}), (ii) appeared to be a single substance, and (iii) was not identical with 2,4,4-trimethyl-1-pyrroline-1-oxide. Hence it is formulated as IX. Furthermore, reaction of the original dimethyl nitrone with phenyl magnesium bromide, followed by dehydrogenation of the product (X), gave the phenyl nitrone (XI), which, when subjected to the oxygen transfer reaction (10) with triphenylphosphine, gave a volatile base that proved to be identical with an authentic sample (11) of 3,3-dimethyl-2-phenyl-1-pyrroline (XII). Alternatively, the hydroxylamine (X) could be directly converted into the pyrroline (XII) by melting it with potassium hydrogen sulfate. It may be noted that the ultraviolet spectrum of XI shows absorption at somewhat lower wavelength and intensity than that of 2-phenyl-1-pyrroline-1-oxide (12). This is attributed to a certain degree of steric inhibition of conjugation analogous to that which has been observed with a series of phenyl ketones (13).



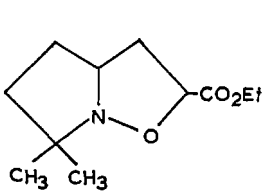
These chemical sequences suggest that the dimethyl nitrone has structure (III), and the proton magnetic resonance spectrum of the base supports this conclusion (1). The absence of the other isomer (IV), in which dehydrogenation has occurred on the least hindered side, is noteworthy. To detect small quantities of this isomer in the product, the sequence (III) → (IX) → trimethylpyrroline was followed, purification at the intermediate and final stages being deliberately avoided. The trimethylpyrroline resulting from this process was examined by vapor phase chromatography, and was shown to consist mainly of a base which had a retention volume different from that of 2,4,4-trimethyl-1-pyrroline, and which was characterized as 2,3,3-trimethyl-1-pyrroline. A small peak which had approximately the same retention volume as 2,4,4-trimethyl-1-pyrroline was indeed present, but amounted to less than 3% of the area of the main peak. It thus appears that dehydrogenation occurs predominantly on the more hindered side of the cyclic hydroxylamine. Two possible interpretations of this result have been considered. Firstly, it is apparent that the nitrone (IV) can undergo self-condensation of the aldol type, whereas III cannot. Hence it might be supposed that both isomers are formed extensively, but that IV is not isolated because it polymerizes. However, it is to be noted that the parent nitrone in this series, 1-pyrroline-1-oxide itself, has been prepared in good yield by this route (7). The second involves the steric effect of the *gem*-dimethyl group, an effect already manifested in certain of the ultraviolet spectra. On the basis of the analogy to the dehydrogenation of N,N-disubstituted hydrazines (14) it is likely that the oxygen function is involved in the initial stages of the reaction: although the process may be further complicated by conformational considerations it would appear reasonable that subsequent reaction proceeds in that direction which will relieve most effectively the non-bonded interactions of C-methyl and C—H bonds, leading to structure III in preference to IV.

The 1-pyrroline-1-oxides are known to undergo cyclo-addition reactions with suitably substituted olefins (15), the adducts possessing the novel 2-oxa-1-azabicyclo[3.3.0]octane ring system (XIII).

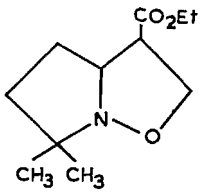


XIII

Thus, for the addition of ethyl acrylate to 5,5-dimethyl-1-pyrroline-1-oxide, evidence has been presented (16) which suggests that the adduct of structure XIV is rapidly formed but that the isomer XV is thermodynamically more stable.

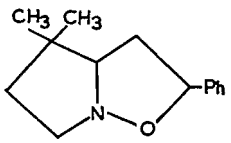


XIV

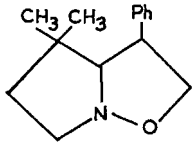


XV

It was of interest to determine whether the nitrone prepared in the present work was subject to this type of addition. Although the yields were only moderate in some instances the cyclo-addition reaction was shown to proceed satisfactorily at temperatures below 100°. The addition of styrene gave a colorless oil which could be satisfactorily purified by distillation under low pressure and which formed a picrate. The infrared and ultraviolet spectra of the adduct were in accord with the bicyclic structure (XVI). A decision between the positional isomers XVI*a* and XVI*b* could be made on the basis of the proton magnetic resonance spectrum, since in XVI*a* the proton at C3 is subject to two deshielding influences and would be expected to be brought into resonance at relatively low field (cf. $PhCH_2OH$ at 5.6 τ (17)), whereas in the isomer there is no similar compounding of deshielding effects. The spectrum of the base did, in fact, show a signal corresponding to one proton at 5.04 τ, and this was assigned to the proton at C3 in structure XVI*a*.



XVIa

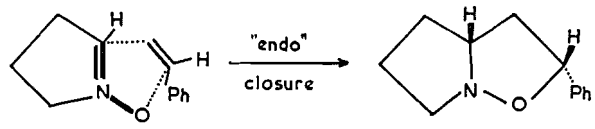


XVIb

Since this signal took the form of a triplet, the coupling constants between the C3 proton and the protons at C4 would appear to be fortuitously similar or to be subject to an averaging process (cf. the triplet assigned to the anomeric hydrogen in thymidine (18): the positions of the other signals supported structure XVI*a*, as did the ratios of their areas. That the steric effect of the *gem*-dimethyl group was not primarily responsible for the direction of addition observed to predominate was shown by examining the adduct of styrene and 5,5-dimethyl-1-pyrroline-1-oxide. Again the proton magnetic resonance spectrum showed a signal in the 5 τ region, and it was concluded that addition had occurred in the same sense as in the previous example. The same orientation has been observed in the addition of styrene to benzylidene aniline N-oxide (19).

When it arises the question of configuration at C3 (or C4) has not been settled for any of the 2-oxa-1-azabicyclo[3.3.0]octanes made in this way. Thus in the present examples the two possibilities are indicated in structures XVI*c* and XVI*d*, each being a racemate. The analogous problem in the Diels–Alder reaction has sustained a good deal of attention, and since the *cis* mode of addition has been demonstrated for several examples of 1,3-dipolar addition (19) it remains of particular interest to determine to what extent, if any, considerations analogous to the "rule" of endo-addition (leading to XVI*d*) also apply.

XVIc



XVId

It is pertinent that electron-accommodating substituents at the alkene linkage are not strictly necessary for nitrone addition to proceed in satisfactory yield (15, 19, 20) and that the 1,3-dipolar group, being smaller in extent than the 1,3-diene system, will be less likely to interact directly with such a substituent in the transition state.

EXPERIMENTAL

The following equipment was used. Melting points: Fisher-Johns heated block. Infrared spectra: Perkin–Elmer Infracord or Model 21. Vapor phase chromatography: Aerograph model A-100-C. Proton magnetic resonance spectra: Varian A60; dilute solutions in carbon tetrachloride: tetramethylsilane internal reference. Analyses by Dr. A. Bernhardt, Mulheim.

1-Ethyl-3,3-dimethylpyrrolidine (VII)

$\alpha\alpha$-Dimethylsuccinic acid (257 g) (21) was treated with aqueous ethylamine (50%; 450 ml) and gradually heated to 200° under a short air condenser. After 15 min at this temperature the product, 1-ethyl-3,3-dimethylsuccinimide, was distilled as a colorless liquid, (207 g, 76%), b.p. 110° at 24 mm, η_D^{20} 1.4605.

Found: C, 61.5; H, 8.0; N, 9.4. $C_8H_{13}NO_2$ requires C, 61.9; H, 8.4; N, 9.0.

The imide was reduced in tetrahydrofuran with lithium aluminium hydride in the normal way (21) to give 1-ethyl-3,3-dimethylpyrrolidine (65%) b.p. 127° at 746 mm as a colorless liquid, η_D^{20} 1.4280. Infrared maxima (film) at 2 778, 1 372, and 1 359 cm^{-1}.

Picrate from ethanol, m.p. 165°. Found: C, 47.6; H, 5.7; N, 15.8. $C_{14}H_{20}N_4O_7$ requires C, 47.2; H, 5.7; N, 15.7.

1-Hydroxy-3,3-dimethylpyrrolidine (VI)

1-Ethyl-3,3-dimethylpyrrolidine (63.2 g) was carefully added, with stirring, to hydrogen peroxide (30%; 295 g) cooled in ice so that the internal temperature did not exceed 60°. The mixture was stirred for 24 h. A pinch of platinum black was added and the mixture stirred at room temperature for a further 24 h. Any unchanged amine was extracted with ether, and the resulting aqueous solution was concentrated to an oily liquid, the last traces of water being removed by codistillation with benzene. The picrate, m.p. 135°, of 1-ethyl-3,3-dimethylpyrrolidine-1-oxide was prepared in water and recrystallized from ethanol.

Found: C, 45.1; H, 5.3; N, 15.2. $C_{14}H_{20}N_4O_8$ requires C, 45.15; H, 5.4; N, 15.05.

The amine oxide was pyrolyzed in small portions (7) in an oil bath at 145° and at a pressure of approximately 10 mm. Under these conditions 1-hydroxy-3,3-dimethylpyrrolidine slowly distilled as a pale yellow liquid with an apparent b.p. of 71–74° and in an overall yield of 34–45% based on the tertiary amine. The infrared absorption spectrum (film) showed no band at 2 770 cm^{-1}, a very weak peak at 1 582 cm^{-1}, and a strong band at 3 226 cm^{-1}. The hydrogen oxalate, m.p. 125°, was prepared in acetone and recrystallized from methanol–water.

Found: C, 47.05; H, 7.2; N, 7.1. $C_8H_{15}NO_5$ requires C, 46.8; H, 7.4; N, 6.8.

3,3-Dimethyl-1-pyrroline-1-oxide (III)

The hydroxylamine (3.6 g) in anhydrous chloroform (85 ml) was treated with yellow mercuric oxide (13.5 g) and shaken for 2 h. Another portion of mercuric oxide (3.5 g) was then added, and, after 2 more hours of shaking, the grey-green mixture was filtered (Celite) and the pad washed with a little chloroform. The solvent was removed, and the residual oil was kept in the dark over phosphorus pentoxide for 72 h.

Distillation gave 3,3-dimethyl-1-pyrroline-1-oxide (2.2 g, 62%) as a hygroscopic oil, b.p. 74–76° at 0.55 mm. It solidified, on cooling, to a mass of long needles, m.p. ca. 25°, and was stored at −20°.

Found: C, 62.5; H, 9.4; N, 12.1. $C_6H_{11}NO$ requires C, 63.7; H, 9.8; N, 12.4.

The picrate, m.p. 105° from ethanol. Found: C, 42.2; H, 4.35; N, 16.4. $C_{12}H_{14}N_4O_8$ requires C, 42.1; H, 4.1; N, 16.4.

The infrared spectrum of the nitrone (film) showed peaks at 3 460 (broad) and 1 580 cm^{-1} (strong). The ultraviolet spectrum: in hexane λ_{max} 248 mμ (log ϵ 3.98); in ethanol λ_{max} 235 mμ (log ϵ 3.93). On continued irradiation with ultraviolet light these absorbancies fell sharply.

Methylation Experiments

3,3-Dimethyl-1-pyrroline-1-oxide (1.29 g) in dry ether (15 ml) was added to methyl magnesium iodide (from 0.35 g magnesium) in 25 ml dry ether and then heated under reflux for 1 h. After decomposition with aqueous ammonium chloride, the product was isolated in ether. The ether solution was dried and evaporated to yield 1-hydroxy-2,3,3-trimethylpyrrolidine as an oil. This was dissolved in dry dichloromethane (30 ml) and treated with yellow mercuric oxide (portions of 4.8 g and 1.2 g) as in the previous oxidation experiment. Isolation of the product gave 2,3,3-trimethyl-1-pyrroline-1-oxide (IX) (0.64 g, 44%) as an oil, b.p. 62° at 0.17 mm, which, on cooling, formed very hygroscopic needles. Infrared spectrum (film); 3 436 cm^{-1} (moisture), 1 610 cm^{-1} (C═N → O): ultraviolet spectrum; in methanol λ_{max} 229 mμ, (log ϵ 3.96).

The picrate, m.p. 174°, needles from ethanol.

Found: C, 43.8; H, 4.7; N, 15.6. $C_{13}H_{16}N_4O_8$ requires C, 43.8; H, 4.5; N, 15.7.

Repeated fractional crystallization of the total picrate preparation did not yield an isomeric picrate.

In a second series of experiments, the above steps were repeated starting with 0.4 g of the dimethyl nitrone, but the trimethyl nitrone was not purified by distillation. Instead the crude oily product was heated (free flame) with triphenylphosphine (1 g) for 5 min before the volatile base (0.15 ml) was distilled out. This basic liquid was submitted to purification by vapor phase chromatography (Aerograph instrument, 5 ft Ucon polar column at 95°, helium carrier gas at 100 ml/min). Under these conditions 2,4,4-trimethyl-1-pyrroline exhibited a retention volume of 590 ml. The product from the oxygen-transfer reaction showed a small response at retention volume 580 ml, and a major one at retention volume 750 ml. The ratio of the areas was 1:34. The 2,3,3-trimethyl-1-pyrroline represented by the second peak was collected. Infrared absorption (film) occurred at 1 637 cm^{-1}. The picrate, tiny prisms, m.p. 249–251° (decomp.), from ethanol was analyzed.

Found: C, 46.0; H, 4.5; N, 16.5. $C_{13}H_{16}N_4O_7$ requires C, 45.9; H, 4.7; N, 16.5.

3,3-Dimethyl-2-phenyl-1-pyrroline (XII) from 3,3-Dimethyl-1-pyrroline-1-oxide

(i) Addition of Phenyl Magnesium Bromide

3,3-Dimethyl-1-pyrroline-1-oxide (1 g) in ether (10 ml) was added to phenyl magnesium bromide (from 3 g phenyl bromide) in ether (20 ml), heated under reflux for 1 h and treated with aqueous ammonium chloride. The ether layer was washed with water, dried, and concentrated. Addition of hexane caused 1-hydroxy-3,3-dimethyl-2-phenylpyrrolidine (0.97 g, 57%) to crystallize out as small prisms, m.p. 129°. Recrystallization of a small sample from ether/hexane raised the melting point to 130°.

Found: N, 7.55. $C_{12}H_{17}ON$ requires N, 7.3.

(ii) Dehydrogenation

The hydroxylamine (0.9 g) was stirred in 25 ml dichloromethane with yellow mercuric oxide (5 g) for 3 h. Filtration, drying, and concentration gave an oil which crystallized on cooling (0.71 g, 79%). A small portion of the 3,3-dimethyl-2-phenyl-1-pyrroline-1-oxide was distilled (hot box, 115° at 0.2 mm) and showed a new band in the infrared (film) at 1 534 cm^{-1}. The ultraviolet spectrum (ethanol) had λ_{max} 283 mμ (log ϵ 3.83).

The picrate, m.p. 137°, light-sensitive prisms from ethanol.

Found: C, 51.6; H, 4.5; N, 13.2. $C_{18}H_{18}N_4O_8$ requires C, 51.7; H, 4.3; N, 13.4.

(iii) Oxygen Transfer

3,3-Dimethyl-2-phenyl-1-pyrroline-1-oxide (0.5 g) was heated with 1 g of triphenylphosphine (free flame) for 5 min. A volatile liquid was formed which was distilled off at 125–135° at 15 mm. The infrared spectrum of the liquid was essentially identical with that of authentic 3,3-dimethyl-2-phenyl-1-pyrroline (11). The picrate (0.46 g, 43%) was prepared in ether and recrystallized from ethanol.

M.p. and mixed m.p. 161° (lit. (11) 160°).

Found: C, 53.4; H, 4.5; N, 13.9. $C_{18}H_{18}N_4O_7$ requires C, 53.7; H, 4.5; N, 13.9.

(iv) The Direct Dehydration of the Hydroxylamine (X)

1-Hydroxy-3,3-dimethyl-2-phenylpyrrolidine (0.32 g from (i)) and potassium hydrogen sulfate (0.4 g) were mixed and heated for 1 h in a stoppered tube in an oil bath at 150–155°. Water was added to the warm dark-brown product, which was treated with aqueous sodium hydroxide, and extracted with ether. The ether was washed with water, heated under reflux with charcoal, filtered, and treated with picric acid in moist ether. This gave 0.19 g (28%) of 3,3-dimethyl-2-phenyl-1-pyrroline picrate, m.p. 158–159°, raised to 160–161° on one recrystallization from ethanol. Mixed m.p. 160–161°.

Reduction of 3,3-Dimethyl-1-pyrroline-1-oxide to 3,3-Dimethylpyrrolidine

To lithium aluminium hydride (1 g) in ether (70 ml) was added 3,3-dimethyl-1-pyrroline-1-oxide (0.5 g) in ether (10 ml). The mixture was refluxed for 1 h. Aluminium chloride (anhydrous, 1 g) was then added and the mixture heated under reflux for a further hour. Decomposition with 30% aqueous sodium hydroxide followed by treatment of the separated, washed ether layer with ethereal picric acid gave a precipitate of yellow needles (0.90 g, 62%) m.p. and mixed m.p. 160°.

Analytical sample from ethanol.

Found: C, 43.8; H, 4.8; N, 16.8. $C_{12}H_{16}N_4O_7$ requires C, 43.9; H, 4.9; N, 17.1.

Dipolar Addition Reactions

(i) 6,6-Dimethyl-3-phenyl-2-oxa-1-azabicyclo[3.3.0] octane (XVIa)

3,3-Dimethyl-1-pyrroline-1-oxide (0.5 g) was heated with styrene (2.5 ml) on the steam bath for 20 h. Distillation (hot box; 135° at 0.35 mm) gave the adduct (XVI*a*) as a colorless oil (0.7 g, 73%) with η_D^{20} 1.5345.

Found: C, 77.0; H, 8.6; N, 6.9. $C_{14}H_{19}NO$ requires C, 77.4; H, 8.8; N, 6.45.

λ_{max} (ethanol): 258 mμ, log ϵ 2.45. ν_{max} (film) at 1 595, 1 484, 1 377, 1 359 cm^{-1}. The n.m.r. spectrum (CCl_4 solution, τ values): 2.82 (Ph); 5.04 (Ph—C*H*—O); ~6.81 (NCH); and 7.62–8.57, 8.93 (CH_2 and CH_3) with relative areas of 5.0, 0.95, 3.09, and 10.6 respectively.

The picrate, recrystallized from ethanol, had m.p. 153°.

Found C, 53.9; H, 4.9; N, 12.8. $C_{20}H_{22}N_4O_8$ requires C, 53.8; H, 5.0; N, 12.55.

(ii) 8,8-Dimethyl-3-phenyl-2-oxa-1-azabicyclo[3.3.0] octane

5,5-Dimethyl-1-pyrroline-1-oxide (1 g) in styrene (5 ml) was heated on the steam bath for 8 h. Distillation gave 1.74 g (90%) of the adduct as a colorless liquid, b.p. 98–100° at 0.1 mm., η_D^{20} 1.5335.

Found: C, 77.3; H, 8.7; N, 6.6.

λ_{max} (ethanol): 258 mμ, log ϵ 2.44. ν_{max} (film) 1 603, 1 493, 1 379, 1 364 cm^{-1}. The n.m.r. spectrum (CCl_4 solution, τ values): 2.81 (Ph): 5.13 (Ph—C*H*—O); ~6.20 (NC*H*); and 7.65; 7.86–8.60; 8.69; 8.99 (CH_2 and CH_3) with relative areas of 5.0, 0.97, 1.08, and 12.4 respectively.

The picrate, from ethanol, had m.p. 175°. Found: C, 53.6; H, 4.9; N, 12.8.

ACKNOWLEDGMENTS

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