

DEAMINATION OF SOME CARANAMINES

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In view of current interest in the chemistry of the caranamines^(1,2) we now describe our work on the deamination of the caranamines (I-III; R=NH₂; R¹=Me),⁽²⁾ which has reached an advanced stage, and we comment on some of the results obtained.

In a typical experiment, amine (1 mole) in 2N sulphuric acid (3 mole) was treated at 0° during 15 min. with aqueous sodium nitrite (27%; 6 mole), and stirring was continued for a further 12 hr. The products were analysed by gas-liquid chromatography (g.l.c.) on Carbowax and Castorwax columns, and in most cases they were isolated by preparative g.l.c. and identified by comparison with authentic material and/or by spectroscopy. Deamination products with their approximate relative amounts (average of several experiments) are given in Table I.

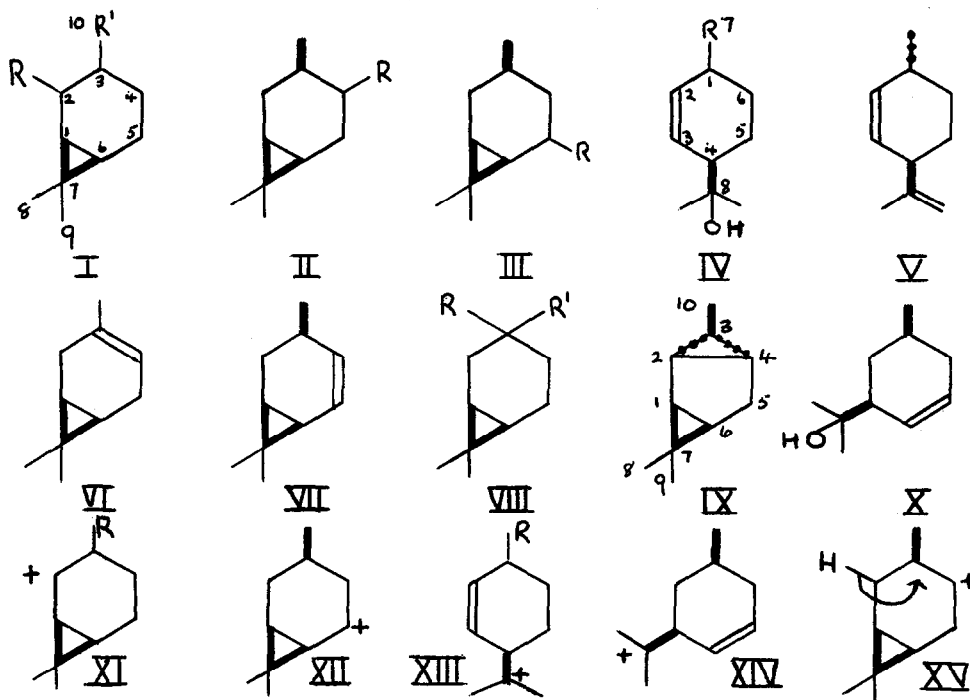
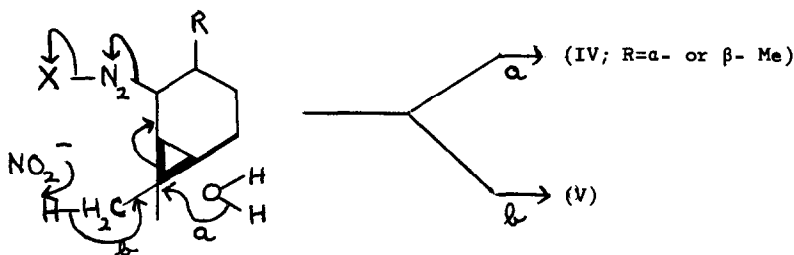


TABLE I
Products of Deamination of Caranamines

<u>Amine</u>	<u>Product</u>
(I; R= α -NH ₂ ; R' $=\beta$ -Me)	(I; R= α -OH; R' $=\beta$ -Me) ³ (24) (IV; R= β -Me) (51)
(I; R= β -NH ₂ ; R' $=\alpha$ -Me)	(I; R= α -OH; R' $=\alpha$ -Me) ^{3,5} (14) (IV; R= α -Me) ⁵ (42)
(II; R= β -NH ₂)	(VII) (VIII; R= α -OH; R' $=\beta$ -Me) ⁷ (4) (VIII; R= β -OH; R' $=\alpha$ -Me) ⁷ (15)
(II; R= β -OH) ⁴	(II; R= α -OH) ⁴ (IX) (I) Unidentified alcohol (A) (15)
(VI) (32)	(VII) (VIII; R= α -OH; R' $=\beta$ -Me) ⁷ (14) (VIII; R= β -OH; R' $=\alpha$ -Me) (6) (II; R= β -OH) (19)
(II; R= α -OH)	(IX) (I) Unidentified alcohol (A) (15)
(III; R= β -NH ₂)	(III; R= β -OH) ⁴ (6) (III; R= α -OH) ⁴ (6) (X) ^{5,8} (81) Other hydrocarbons (8)
(III; R= α -NH ₂)	(III; R= β -OH) (7) (III; R= α -OH) (8) (X) (85) Other hydrocarbons (3)

The initial pseudo-allylic carbonium ions (XI; R= α - or β - Me) and (XII), derived from the caran-2- and 5- amines, rearrange to the tertiary ions (XIII; R= α - or β - Me) and (XIV) respectively, all ions presumably being solvated. Whilst the electronic effects operating on each pair of carbonium ion systems are likely to be finely balanced, the driving force in the formation of the tertiary ions is probably the release of steric strain present in the cyclic ions. The tertiary ions are presumably formed very rapidly; formation of substantial amounts of (IV; R= α - or β - methyl), (V) and (X) follows. (-)-cis-p-Menth-2-en-8-ol (IV; R= β - Me), a new compound obtained in 90% purity (g.l.c.), shows peaks in its n.m.r. spectrum (60 Mc./sec.) at τ 4.33 (2 olefinic protons), 6.42 (OH, removed by D₂O), 8.85 and 8.89 (singlets, oxyisopropyl) and 9.02 (doublet, J=6c./sec., 7- methyl).

It is possible that the menthadiene and menthenols are formed by an assisted reaction, not involving carbonium ions,⁽⁹⁾ as shown below for the 2- amine. Such a mechanism would be particularly appropriate for the 2 α - and 5 α - amines where the geometry is favourable.⁽²⁾



The menthane derivatives are primary deamination products. They are not formed from the caran-2- or 5- ols under deamination conditions although these alcohols do afford menthadienes or menthenols under appropriate conditions of acidity.⁽⁵⁾

The carbonium ion (XV) or equivalent species,⁽⁹⁾ derived from the 4- amine either undergoes loss of proton from its adjacent carbon atoms giving the carenes (VI) and (VII), or hydride transfer from the adjacent tertiary carbon giving a more stable ion from which car-3-ene (VI) and the caran-3-ols (VIII; R= α - or β - OH; R'= β - or α - Me) are derived, whilst electron transfer from the pseudo-allylic 2- position gives the new hydrocarbon (IX). This has the following properties: - $[\alpha]_D^{25} + 68.4^\circ(\text{CHCl}_3)$; m/e 136 (M^+), 107 ($M^+ - C_2H_5$), 93 ($M^+ - C_3H_7$, base peak), as expected for the two cyclopropane systems; ν_{\max} (liquid) 1046, 862, 815 and 776 cm^{-1} ; τ (100 Mc./sec.) 8.21 (multiplet, CH₂), 8.97 and 9.11 (singlets, gem dimethyl group), 9.05 (doublet, J=6c./sec., 10- methyl group), 8.91

and 9.2 (masked multiplets, 2 cyclopropyl protons), 9.41 (multiplet, 2 cyclopropyl protons), 9.65 (multiplet, 1 cyclopropyl proton). Models show that in (IX) only a trans arrangement of the two cyclopropane rings is sterically permitted. Furthermore since it is unlikely that carbon-3 participates in its formation it has the 10- β -methyl configuration. Moreover this is the more stable of the two possible configurations.

The alcohol (A) which is formed in reasonably good yields, but is difficult to separate from the alcohols (II; R= α - and β - OH), is being investigated further. Deaminations in acetic acid are also in progress.

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