

Rearrangement of Pinane Derivatives. Part 8.¹ Deamination of 2 α H-Pinan-3 α -ylamine

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Solvolysis of 2 α H-pinan-3 α -yl toluene-*p*-sulphonate has been shown to proceed with concomitant 1,2-hydride shift to give the pinan-2-yl carbocation. Contrary to earlier reports, this species reacts normally to give, in good yield, pinan-2-yl substitution products. In contrast the pinan-3-ylamines react *via* a similar route, but give much smaller amounts of pinan-2-yl products. The usual reasons for differences between solvolysis and deamination (*i.e.* the intermediacy of diazonium ions and/or high-energy ions) can be discounted, and possible reasons for the differences in behaviour are discussed.

In an earlier Part,² we reported on the solvolysis of the *cis*- and *trans*-pinan-2-yl *p*-nitrobenzoates (I) and (II) which yielded 30–40% of unrearranged methyl ethers, together with alkenes and ring-opened products. In contrast to these observations Huckel³ studied the solvolysis of the pinan-3-yl toluene-*p*-sulphonates, and reported that reaction proceeds through the pinan-2-yl cations (III) and (IV) generated by a 1,2-hydride shift, but yields only products of elimination and ring opening. Similar observations were made by Jones,⁴ studying deamination of the pinan-3-ylamines. Again, reaction proceeded *via* the pinan-2-yl cation, but no substitution products of the unrearranged system were observed. We have, therefore, investigated this difference of behaviour of the pinan-2-yl cation generated under differing conditions.



RESULTS AND DISCUSSION

Methanolysis of 2 α H-pinan-3 α -yl toluene-*p*-sulphonate at 35 °C was found to be first-order in ester. The effect of adding methoxide ions to the solution was to produce only a small increase in rate, suggesting that the reaction is a unimolecular solvolysis (Table 1). A product study

TABLE 1

Solvolysis of 2 α H-pinan-3 α -yl toluene-*p*-sulphonate (0.031M) in methanol at 35 °C

[NaOMe]/M	10 ⁻⁴ <i>k</i> ₁ /s ⁻¹
0	1.10
0.033	1.60
0.048	1.28

was therefore carried out, using 0.031M-ester in methanol containing 0.033M-sodium methoxide at 35 °C. The results are reported in Table 2, and are compared with our² earlier results on pinan-2 α -yl *p*-nitrobenzoate, and the previously reported³ data on the methanolysis of 2 α H-pinan-3 α -yl toluene-*p*-sulphonate.

Clearly, our results on the 2- and 3-esters are consistent,

while earlier data differ in the absence of the two pinan-2-yl ethers. We therefore repeated the earlier work, under the exact experimental conditions reported (refluxing the ester with methanol in the presence of an excess of calcium carbonate) and obtained exactly the same results as those reported.³ The most likely

TABLE 2

Products of methanolysis of pinanyl esters

Product	% from 2 α H-pinan-3 α -yl toluene- <i>p</i> -sulphonate		% from pinan-2 α -yl <i>p</i> -nitrobenzoate
	Previous	This work	
α -Pinene	17.5	25	33
Camphene	4.0	3	1
Limonene	8.5	8	4
Terpinolene	8.6	2	3
<i>p</i> -Cymene		2	
Bornyl methyl ether	5.0	2	2
Fenchyl methyl ether	12.0	3	3
Pinan-2 α -yl methyl ether		28	25
Pinan-2 β -yl methyl ether		5	3
α -Terpinyl methyl ether	44.7	18	13

explanation for the observed differences is decomposition of the pinan-2-yl ethers under the reaction conditions, so we prepared methyl pinan-2 α -yl ether, and repeated the decomposition of the ester in methanol with calcium carbonate in the presence of this ether. On completion of the reaction, we found that all the ether had decomposed. We conclude that the method described does not give kinetic control of product formation.

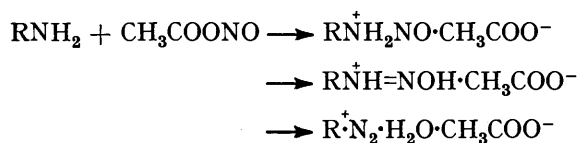
The absence of pinan-2-yl substitution products has also been noted by Jones,⁴ studying the deamination of the pinan-3-ylamines. We therefore repeated the work of Jones. 2 α H-Pinan-3 α -ylamine was deaminated in acetic acid, but our results were in good agreement with those of Jones, and we did not observe either of the pinan-2-yl acetates. We checked product stability by preparing pinan-2 α -ol and pinan-2 α -yl acetate (which should be the less stable isomer²) and adding these substances, plus 1,2,3-trimethylbenzene as internal standard, to a deamination of 2 α H-pinan-3 α -ylamine

TABLE 3
Products of deamination of 2 α H-pinan-3 α -ylamine

Products	Deamination with sodium nitrite in acetic acid at 25 °C	Deamination with acetyl nitrite in acetic acid at 25 °C	Results obtained by Jones ⁴ deamination in aqueous nitrous acid
α -Pinene	3	4	19
Camphene	7	4	10
β -Pinene	1		
Limonene	15	4	4
Terpinolene			1
α -Fenchyl acetate	6	12	
α -Fenchol	1	1	11
Pinan-2 β -ol	1		
Pinan-2 α -ol	3	13	
Bornyl acetate	8	12	
Borneol		1	9
2 α H-Pinan-3 α -yl acetate	1	1	
2 α H-Pinan-3 α -ol			9
α -Terpinyl acetate	41	4	
α -Terpineol	8	34	20

under normal conditions. On completion of reaction, and normal work-up, g.l.c. revealed the ratio of acetate to alcohol to internal standard was unchanged by the reaction. The products of deamination are given in Table 3.

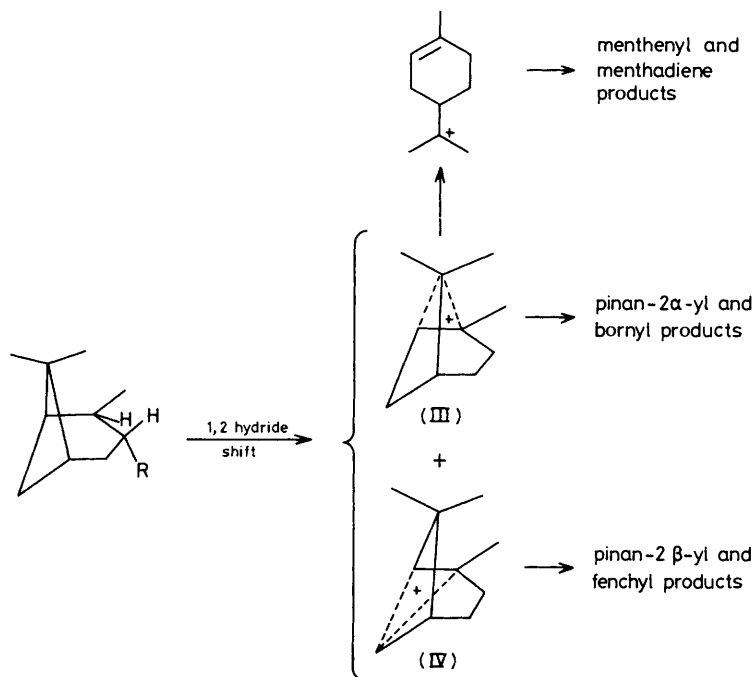
Deamination with sodium nitrite in acetic acid has been suggested by Collins ⁵ to proceed by initial formation of acetyl nitrite, followed by nitrosation of the amine, and rearrangement:



The different product composition observed when acetyl nitrite ⁶ is used as the reagent rather than sodium nitrite suggests that this picture is oversimplified. It does, however, show how a molecule of water is generated in close contact with the diazonium ion RN_2^+ and with the carbocation R^+ so that capture of the water molecule by the intermediate can yield alcohol products.

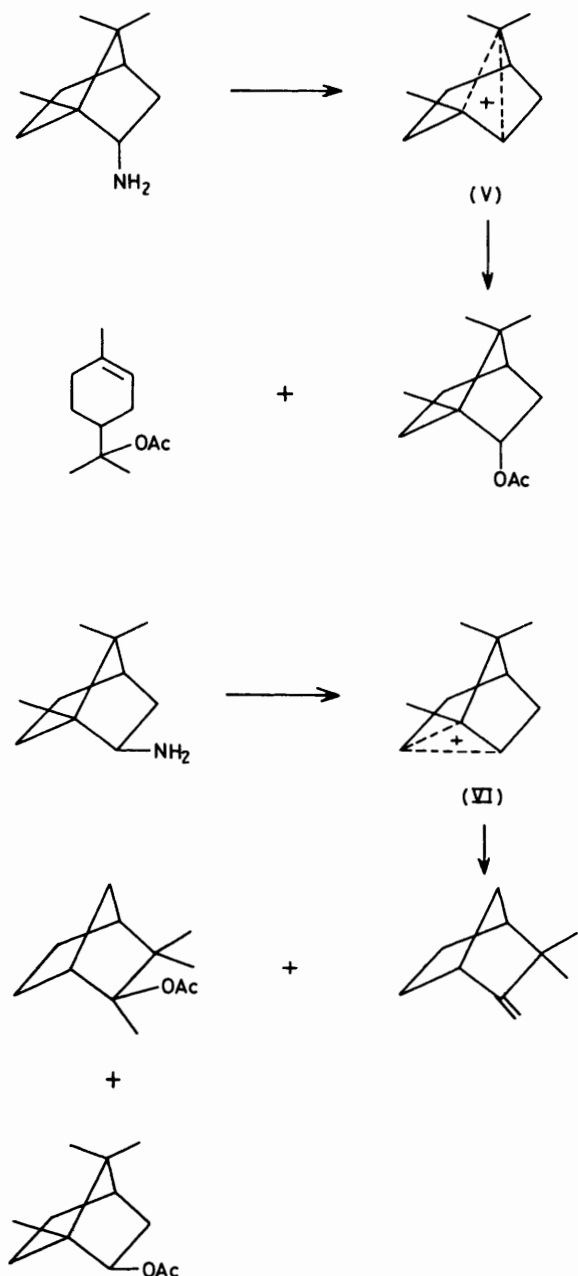
Although the product compositions reported by Jones are accurate, discussion of the results by comparison with the thermodynamically controlled products of toluene-*p*-sulphonate solvolysis is invalid, and must be reconsidered. The important difference between the two sets of results is the absence in the deamination products of the pinan-2-yl substitution products observed in solvolysis. These clearly arise from an initial 1,2-hydride shift, as do almost all the products of both reactions. The overall reaction scheme is summarised in Scheme 1.

Differences in product composition between solvolysis and deamination are usually attributed to exceptional behaviour in deamination, described in terms of a high-energy carbocation,⁷ to compression of the energy profile,⁸ or to reaction of the diazonium ion.⁹ However, examples quoted often compare primary alkyl systems, where a bimolecular solvolysis, or a rate-determining hydride shift, is compared with deamination; in many cases, it is impossible to be certain whether or not there is a diazonium ion contribution to the deamination reaction. In the case which we are considering, the products arise from an ion generated by a 1,2-hydride shift, which should exclude reaction of a diazonium ion in the product-determining step but should also ensure that a high energy or 'hot' carbocation has 'lost most if not all of its sizzle'.¹⁰



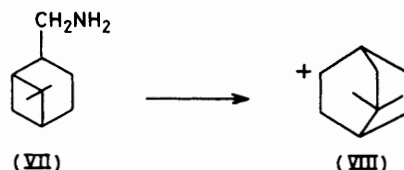
SCHEME 1

The results in Table 2 show that for ion (III), the ratio of substitution reactions at C-2 : C-1 is 28 : 2. During deamination, which almost certainly proceeds through ion (III), since reaction at C-1 is stereospecific whereas reaction of a non-delocalised ion would favour formation of isobornyl, not bornyl, acetate, substitution at C-1 is 12% of the total while substitution at C-2 is absent. We cannot, then, argue that ion (III) generated during deamination is a highly reactive species which undergoes ring opening instead of substitution. Equally, it is difficult to argue that the reaction energy profiles have been modified, since they would have to exclude only reaction at a tertiary centre.



SCHEME 2

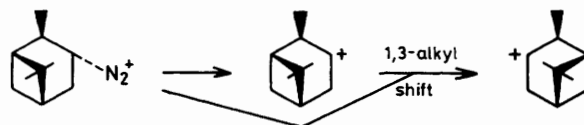
The results are consistent with reaction at C-2 being blocked by something, preventing access of nucleophile to a hindered area. Since deamination yields pinan-2-ol, it follows that the water molecule generated in deamination remains close to the carbocation centre when the 1,2-hydride shift occurs, so it seems likely that the nitrogen molecule is also occupying a critical position. There is no evidence that bonding has occurred to



generate a rearranged diazonium ion, but it is not possible to prove that this has not occurred either.¹¹ The nitrogen could equally well be trapped, together with the water molecule, by the acetate counterion, so that access to C-2 by external nucleophiles is restricted, while reaction with trapped water is favoured. Attack of a nucleophile at C-1 would then form the C-2-C-7 bond, displacing the counterion, nitrogen, and water, or ring opening would migrate the charge to C-7 taking along at least the water molecule.

It is interesting to compare our data with the earlier work of Banthorpe and his co-workers on deamination of the bornylamines.¹²

As shown in Scheme 2, reaction *via* ion (V) [= ion (III)] gives bornyl and terpinyl products; however, reaction *via* (VI) proceeds at both the secondary and tertiary centres, but ring opening does not take place. Clearly, ring opening competes with reaction at the tertiary centre only when the *gem*-dimethyl group stabilised the ring-opened ion. Inhibition of reaction at the tertiary centre, discussed earlier, would favour ring opening, but when that reaction is itself energetically unfavourable, reaction ultimately takes place at the tertiary centre.



When we deaminated 2 α H-pinane-10-ylamine (myrtanylamine) (VII), we found that one of the competing modes of reaction was a 1,3-alkyl shift,¹³ giving ion (VIII). In pinane-3 α -ylamine, the relationship between the leaving amine and the four-membered ring is very similar to that of the 10-amine. A 1,3-alkyl shift, however, would not give any structurally new products from the pinane-3-yl cation, since it would simply invert the ion. We therefore repeated the deamination, using optically active 2 α H-pinane-3 α -ylamine, reduced the α -terpinyl acetate produced to the more thermally stable α -terpinol, and isolated this product. We found that 92% of the optical activity of the starting material was retained in the product, thus setting an upper limit

of 4% of reaction *via* a 1,3-shift. This is of the order of the accuracy of the experiment, and we do not consider it to be significant evidence that this shift reaction does in fact take place. It seems likely that the driving force for the 1,3-alkyl shift in 2 α H-pinane-10-ylamine is relief of ring strain, which force is clearly absent in reactions of the 3-amine.

EXPERIMENTAL

2 α H-Pinan-3 α -yl Toluene-p-sulphonate.—The alcohol prepared from α -pinene as described by Brown¹⁴ was esterified with toluene-*p*-sulphonyl chloride in pyridine for 24 h at room temperature.¹⁵

2 α H-Pinan-3 α -ylamine.—Preparation by hydroboration and reaction with hydroxylamine *O*-sulphonic acid followed the method of Brown.¹⁶

Acetyl Nitrite.—Nitrosyl chloride (3 ml) was condensed into a 100 ml flask, then cooled in a liquid nitrogen bath with swirling so that the nitrosyl chloride solidified on the walls of the flask. Powdered silver acetate was added, then the mixture allowed to warm to room temperature with stirring. After 10 min at room temperature, the flask was cooled to liquid nitrogen temperature, placed on a vacuum line, and evacuated. It was again allowed to warm up, and the acetyl nitrite distilled into a receiver cooled in liquid nitrogen. The product was shown to be free of nitrosyl chloride by hydrolysis and testing for chloride ion. It could readily be destroyed by hydrolysis. Acetyl nitrite is of unknown toxicity and is treated by us as a potential explosive and carcinogen.

Methanolysis Reactions.—These were carried out as described earlier.² Products were analysed by g.l.c., using a 10 ft Carbowax 20 M column.

Deamination Reactions.—Deamination reactions with sodium nitrite in acetic acid were carried out as described earlier.¹³ Reactions with acetyl nitrite were carried out similarly, except that acetyl nitrite replaced the sodium

nitrite. Products were analysed as for methanolysis products.

Determination of Optical Activity of Products.—The starting α -pinene had $[\alpha]_D^{25}$ (EtOH) + 24.35°, compared to the literature value¹⁷ of +48.3°. After hydroboration to the amine and deamination the product was reduced with lithium aluminium hydride, then the α -terpineol isolated by preparative g.l.c. It had $[\alpha]_D^{25}$ (EtOH) + 42.06°, compared to the literature value¹⁷ of +100.5°. Optical rotations were measured on a Thorn-NPL Automatic Polarimeter type 243.

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