

A New Solvolytic Approach to Hydroazulenes

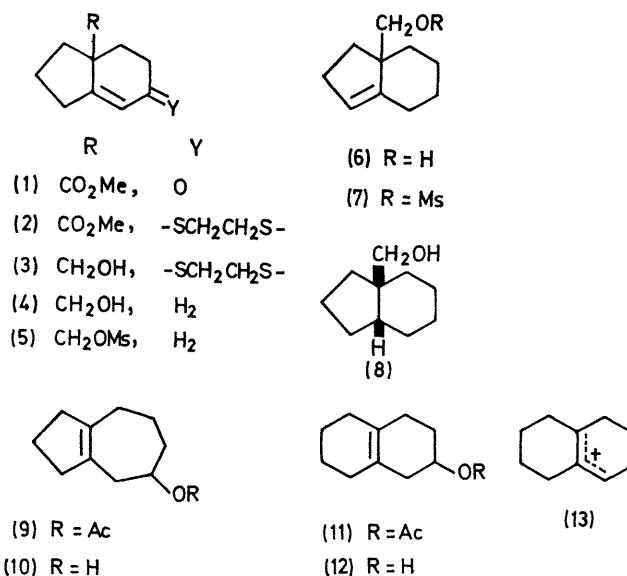
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Summary Solvolysis of a mixture of the methanesulphonates of 3a,4,5,6-tetrahydroindane-3a-methanol (5) and 2,4,5,6,7,7a-hexahydroindene-7a-methanol (7) gave, in high yields, a mixture of 1,2,3,4,5,6,7,8-octahydro-5-azulenyl acetate (9) and 1,2,3,4,5,6,7,8-octahydro-2-naphthyl acetate (11).

THE solvolytic conversion of decalins,¹ bicyclo[4,3,1]-decanes,² and a cyclodecadienol³ into hydroazulenes has recently been reported. These methods, together with the base-induced rearrangement of decalindiol monotonuene-*p*-sulphonates,⁴ have proved to be the only stereoselective synthetic route to hydroazulenic sesquiterpenes. We report an additional solvolytic rearrangement leading to this ring system.

Keto-ester (1)⁵ was converted in essentially quantitative yields into the thioacetal (2)^{6†} [b.p. 145–151°/0.4mm; m.p. ca. 28°; δ (CCl₄, Me₄Si) 5.51 (broad s, 1H, C=CH)] and then, with lithium aluminium hydride, into the hydroxythioacetal (3) [m.p. 85–87°; δ (CCl₄, Me₄Si) 5.51 (broad s, 1H, C=CH)]. Treatment of (3) with W-2 Raney nickel⁷ in ethanol for 15 min at room temperature gave a 60:40 mixture (g.l.c.) of alcohols (4) and (6) [b.p. 75–77°/0.2 mm; m.p. 31.5–33°; δ (CCl₄, Me₄Si) 5.55 (m, 1H, C=CH) 48%]. Alternative structures containing disubstituted double bonds were ruled out on the basis of chemical evidence (*vide infra*) and the presence of only one vinyl proton in the n.m.r. spectrum of the mixture. That desulphurization had not led to unexpected structural



rearrangements was shown by reduction of the mixture of (4) and (6) (PtO₂) to a single compound, the known *cis*-hexahydroindane-3a-methanol (8).⁸

Double-bond migrations are known in the desulphurization of $\alpha\beta$ -unsaturated thioacetals,⁹ but the transformation (3) \rightarrow (6) appears not to have been previously reported. The fact that double-bond migration had occurred during

† Satisfactory combustion analyses were obtained for all new compounds reported.

the desulphurization step was shown by examining the alcohol (3), shown to be homogeneous by chromatography. In addition, the n.m.r. spectrum of (3) is consistent only with a structure in which the vinyl proton is coupled solely to two allylic protons.

Since our primary interest was to study the solvolytic behaviour of homo-allylic alcohols such as (4) and (6), further transformations were carried out on the mixture. The corresponding methanesulphonates (5) and (7) were prepared (MeSO_2Cl , $\text{C}_6\text{H}_5\text{N}$, 4 h) and, without purification, were solvolysed in buffered ($\text{K}_2\text{CO}_3, \text{Ac}_2\text{O}$) acetic acid to a mixture of acetates (9) and (11) [δ ($\text{CCl}_4, \text{Me}_4\text{Si}$) 4.70 (m, 1 H, CHOAc)]. Reduction of the acetates (LiAlH_4) gave a 60:40 (g.l.c.) mixture of alcohols (10) and (12) [88% from the mixture of (4) and (6)]. The structure of this mixture was determined from: (i) $m/e = 152$, (ii) no vinyl or cyclopropyl protons in the n.m.r. spectrum, (iii) rapid decolorization of a $\text{Br}_2\text{-CCl}_4$ solution, (iv) oxidation with $\text{CrO}_3\text{-H}_2\text{SO}_4$

to a mixture of *unsaturated* ketones, and (v) dehydration (KHSO_4 , 150—160°, 45 min) followed by dehydrogenation (Pd-C , 250°, 1 h) to a mixture of azulene and naphthalene.¹⁰ This evidence rules out alternative formulations such as cyclopropylmethanols or allylic alcohols.

Rearrangements of this type are known in steroidal systems¹¹ and in octalins.⁶ To our knowledge, however, they have not been reported in the corresponding hexahydroindanyl systems. In view of the ready ring expansion of perhydroindanyl systems to perhydronaphthalenes¹² our results, in which double-bond participation is the sole mode of rearrangement, are unexpected. A ready rearrangement of either (5) or (7) to the same allylic carbonium ion (13) might have been expected. That this, in fact, did not occur was shown by the absence of either a tri-substituted double bond or an allylic alcohol in either of the solvolysis products.

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