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# The Catalytic Dehydration of Isomeric Octadienols

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THE preparation of substituted hexa-1,3,5-trienes has involved, until recently, either a vapour-phase catalytic dehydration over alumina[1–3] or an acid-catalysed dehydration of an appropriately substituted hexadienol.[4] Substituted trienes obtained by the alumina procedure are usually contaminated with cyclohexa-1,3-dienes formed by on-column electrocyclic ring-closure. Due to ring-closure, trienes having a *cis*-configuration about the 3,4-double bond are rarely observed as products of catalytic dehydration.

Recently we reported[5] that the methylcyclohexa-1,3-dienes obtained as dehydration products from methylhexadienols have structures conforming to the Woodward–Hoffmann rules[6] governing electrocyclic reactions, and the initial stages of catalytic dienol dehydration yield appreciable quantities of labile 3,4-*cis*-isomers, but these readily cyclise in a disrotatory fashion at the temperatures (>200°) employed in most investigations. We now report a new aspect of dienol dehydration.

When octa-2,4-dien-6-ol (I) was dehydrated over alumina at an average column temperature of 240° and the resultant product submitted to g.l.c., at least sixteen compounds were isolated. The major fractions were isolated by trapping techniques from the analytical chromatograph effluent and submitted to i.r., u.v., and n.m.r. spectral analysis. The product consisted of the following: 1,6-dimethylhexa-1,3,5-triene (38%, mixture of three geometric isomers), octa-1,3,5-triene (17%, mixture of two geometric isomers), and dimethyl- and ethyl-cyclohexa-1,3-dienes (34%, mixture of at least four isomeric compounds). Seven unassigned peaks accounted for the remaining 11% of product. Physical constants agreed well with literature values, where available.[3,7] The product composition indicates that the ratio of 1,2- to 1,6-dehydration was approximately 2 : 1.

TABLE

| Octadienol | $Me[CH{=}CH]_3Me$ (% of total) | $Et[CN{=}CH]_3H$ | Cyclohexa-1,3-dienes (5-ethyl or 5,6-dimethyl) |
|---|---|---|---|
| (I) | 38 | 17 | 34 |
| (II) | 30 | 32 | 25 |

Octa-1,3-dien-5-ol (II) was dehydrated under similar conditions at an average column temperature of 245°. As shown in the Table, g.l.c. analysis yielded a chromatogram similar to that of octa-2,4-dien-6-ol. Since only a 1,2-dehydration mode is possible for (II) under "normal" dehydration conditions, the presence of large amounts of octa-2,4,6-triene in the product must be explained either by partial rearrangement of (II) to (I) prior to dehydration, or by rearrangement of octa-1,3,5-triene to octa-2,4,6-triene following dehydration. In the light of previous work[1,3,5] on the dehydration of isomeric hexadienols, we favour the latter argument. In all reported examples, the triene obtained was the one predicted on the basis of simple 1,2-, 1,4-, or 1,6-dehydration. Therefore, we interpret our results to indicate a new aspect to the mechanism of dienol dehydration: on-column rearrangement of a labile intermediate triene to a more stable trienic structure.

The probable sequence of events in a typical catalytic dienol dehydration is:

(1) dehydration to yield an initial trienic mixture; the incipient double bond shows little *cis–trans* preference, and a geometric mixture usually results,[5]

(2) geometric isomers having a *cis*-configuration about the central double bond then undergo electrocyclic ring-closure according to the Woodward–Hoffmann rules yielding substituted cyclohexa-1,3-dienes of predictable structure,[5]

(3) dehydrogenation of cyclohexa-1,3-dienes to yield the corresponding aromatic compound,[8]

(4) triene–triene rearrangement yielding the more stable polyene.

The compounds isolated from our dehydration product can be rationalized as follows: the surviving three geometric isomers of octa-2,4,6-triene, and the two surviving geometric isomers of octa-1,3,5-triene have *trans*-configurations about the central double bond; electrocyclic ring-closure of the isomers containing a *cis*-central double bond results in a mixture of *cis*- and *trans*-5,6-dimethylcyclohexa-1,3-diene, 5-ethylcyclohexa-1,3-diene and 1,6-dimethylcyclohexa-1,3-diene. This last product has been observed by Marvel[7] in electrocyclic ring closure of octa-2,4,6-triene. Although we have been unable to totally resolve this mixture, the u.v. maxima (263, 264, and 233 m$\mu$) are in good agreement with literature values.[2,7]

The mechanism of the octa-1,3,5- to -2,4,6-triene conversion is currently under investigation. It appears probable that proton donation from an active OH site to C(1), followed by proton abstraction from C(7) by an oxygen at a different catalyst site is responsible for this isomerisation.

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