Prototropic Shifts in Conjugated Olefins

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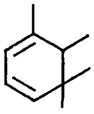
Summary Kinetic control of prototropic shifts can lead to *transoid* conjugated olefins with terminal methylene groups.

DESPITE work on acid-catalysed isomerizations of dienes and polyenes[1] and on their derived cations,[2] the synthetic value of such reactions has been little utilized; in particular few cyclohexenylidenes have been obtained by such methods, and the variation of product with reaction time[3] has been little developed.

We have confirmed the reported[4] isomerization of α-phellandrene to an equilibrium mixture of three isomeric dienes in the proportions given, but have also found that, at 40% conversion, β-phellandrene is the main (50%) product, which is rapidly isomerized further.

Similarly, brief treatment of α-pyronene (**1**)[5] with HCl in $CHCl_3$ gives the diene (**2**), λ_{max} 232 nm, with appropriate i.r. and n.m.r. spectra, while β-pyronene (**3**) and γ-pyronene (**4**) are the main products of intermediate and prolonged treatments, respectively (see Figure). With the same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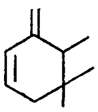
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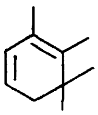
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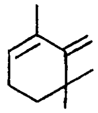
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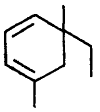
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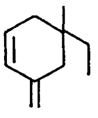
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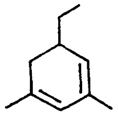
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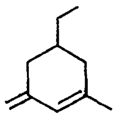
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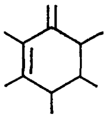
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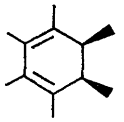
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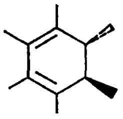

(11)

reagent the cyclohexadienes (**5**)[6] and (**7**)[7] yield the *transoid* dienes (**6**) (23%) and (**8**) (42%) respectively. On the other hand we have been unable to detect any cyclohexenylidene (**9**) at any time during the course of the similar[8] isomerization of the *cis*-hexamethyl analogue (**10**) to the *trans*-isomer (**11**). The formation of (**9**) would involve a reduction from six to four alkyl substituents on the diene system, and in the absence of marked steric or electronic stabilizing factors it seems that such reduction thermodynamically disfavours the heteroannular diene. Kinetically, however, the formation of (**9**) is favoured; the high deuterium incorporation [up to five atoms of deuterium in (**11**) and three in (**10**) as measured by g.l.c.–mass spectrometry] at 25% isomerization of (**10**) to (**11**), indicates the rapid reversible formation of (**9**).

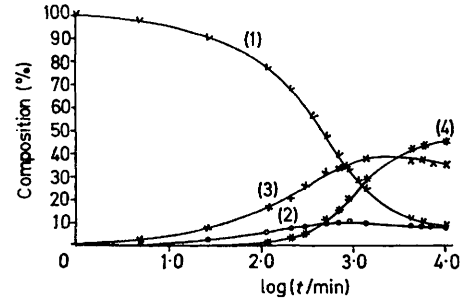
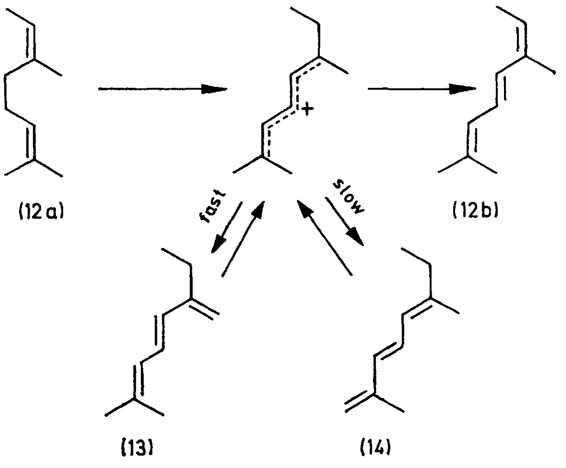


FIGURE. Acid isomerisation of α-pyronene (**1**).

The simple ion-pair intermediate which might[9] be expected under these conditions would lead to rapid deuteriation of only the *cis*-starting material. Either an intermediate allyl carbonium ion, which could take up deuterium by fast reversible formation of the undetected (**9**) (*cf.* camphene[10]), or a more complex series of stereoisomeric ion pairs are in accord with these results. The former possibility is consistent with our finding that brief DCl-catalysed isomerization of 4-*cis*,6-*cis*-alloocimene (**12a**)[11] gives the 4-*trans*,6-*cis*- (**12b**) (10%) and 4-*trans*,6-*trans*- (7%) isomers, both containing up to four atoms of deuterium but with no deuterium incorporated in (**12a**). Treatment overnight gave both isomers (4-*trans*,6-*trans*, 60%; 4-*trans*,6-*cis*, 26%) having 8—10 D atoms (86%), and these, on brief treatment with HCl lost four atoms of deuterium. This indicates a rapid shuttling between the carbonium ion and the triene (**13**), and a slower transient formation of (**14**).[12]



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[12] *Cf.* B. M. Mitzner and E. T. Theimer, *Appl. Spectroscopy*, 1965, **19**, 169. We have prepared both (**13**) and (**14**), and found that neither is present (>1%) in the product. We thank Dr. Theimer for describing the synthesis.