Tetrahedron Letters No. 41, pp 3555 - 3558, 1975. Pergamon Press. Printed in Great Britain.

[1,7]-HYDROGEN SHIFTS IN SIMPLE CONJUGATED TRIENES

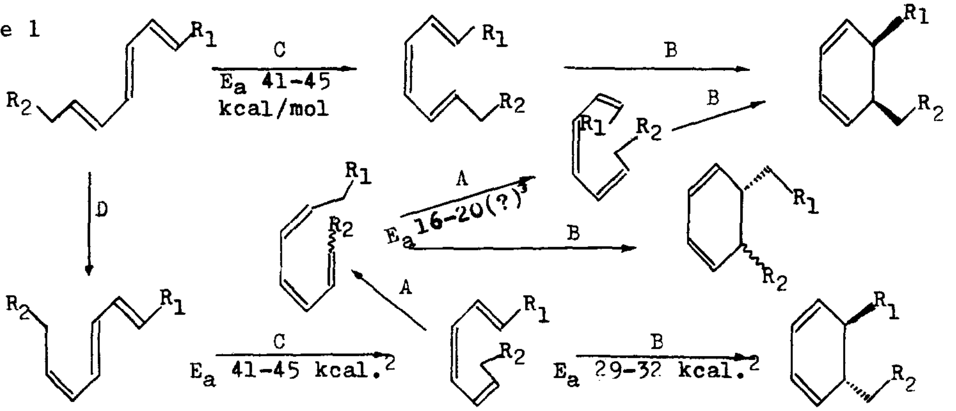
Kevin J. Crowley* and Sean G. Traynor

University Chemical Laboratory, Trinity College, Dublin 2, Ireland

(Received in UK 21st July, 1975; accepted for publication 29th August, 1975)

Despite much detailed work on the thermal isomerization of conjugated trienes, the relative ease of some of the possible reactions (Scheme 1) remains unclear. In particular, although several instances of [1,7]-H shifts have been reported, the scope of the isomerization is uncertain, and doubt has been cast on its occurrence in simple acyclic triene systems.[1] We suggest that in the absence of inhibiting steric or electronic factors the preferred initial thermal reaction in 1,3,5-heptatrienes is a [1,7]-H shift.

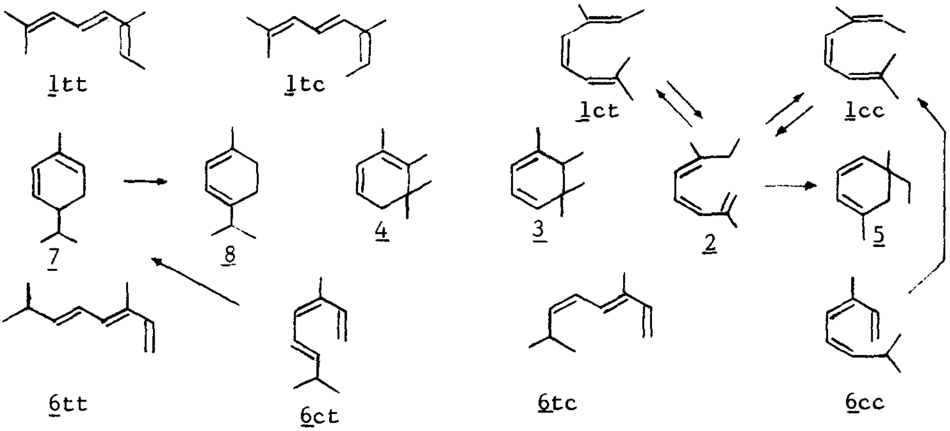
Scheme 1



Most simple trienes which have been subjected to detailed pyrolysis studies have been isomers or mixtures of isomers having the central double bond trans,[2,4,5] and these will rapidly give cyclic products (reaction B) after the energetic reaction C. Thus the course of the reaction will be dictated largely by the relative stabilities of the various possible cyclohexadienes rather than those of the [1,7]-H-shifted intermediates (e.g.

Ref. 1). Several trienes having the necessary *cis*-*cis* geometry have been pyrolyzed to give [1,7]-H-shifted trienes which were either degenerate[6] or less substituted; the latter would normally be unfavoured, having less opportunity for hyperconjugative stabilization, and have been observed only in cases where the more substituted precursor triene is sterically hindered in all planar conformations[7,8] or enjoys reduced conjugative stabilization with substituent π-bonded groups.[3] The occurrence of other [1,7]-H shifts has been demonstrated,[8,9] but the immediate product has not been observed directly in an acyclic compound.

Our interest in this area arises from the ready thermal isomerization of the *cis*-*trans*-alloocimene (**1**ct) to the *cis*-*cis*-isomer (**1**cc) without the formation of the 4-*trans*-isomers.[10] We now report that this is reversible (see Table) and that it probably occurs via the less-substituted triene (**2**) (Reaction A). At higher temperatures (300°) cyclization (Reaction B) sets in, yielding α-pyronene (**3**), which progressively forms the more stable β-pyronene (**4**) by a [1,5]-H shift. The two 4-*trans*-isomers of alloocimene



are stable under these conditions up to 360°, when Reaction C (followed by B) begins; a small amount of Reaction D (**1**tt → **1**tc) set in at about 400° (possibly glass catalyzed, see [2,3]). The formation of the ethyldimethyl

Table

Injection of Block Pyrolyses[a] of 1cc, 6 and 7

Starting material	Block temp. °C	Products[b] - percentage composition												
		3	5	4	7	8	1cc	6cc	6tc	6ct	6tt	1ct	1tc	1tt
triene 1cc[c]							100							
	170						96					2	2	
	230						80					15	3	2
	255						69					23	4	3
	283	2					54					38	3	3
	313	6					49					40	2	1
	335	17	2				43					33	2	2
	360	30	6	3			31					20	5	5
	400	35	11	18			14					5	8	9
	450	20	13	29			1						10	9
	500	2	17	34			1						9	11
trienes 6							0[d]	20	22	24	21			
	180						4	18	21	23	22			
	245				2		12	6	21	24	21	2		
	285				9		9		21	17	21	11		
	340	2			25		5		20		20	16		
diene 7					75[e]									
	360				62	13								
	395				44	31								
	456				7	68								

a. In the glass-lined injection block of a Perkin-Elmer F 11 gas chromatograph; residence time about 0.5 sec.

b. In order of elution from a Carbowax 20M column: similar results were obtained using a squalane capillary column (100 m), and by heating the mixture of trienes (6) in glass vials at 100° and 150° as previously described for 1.[10] Trienes (6) were identified by their relative rates of formation during irradiation while trienes 1 were previously characterized.[10]

c. An internal standard (p-cymene) showed the absence of any significant loss.

d. An unidentified impurity (12%) in the starting material, having the same retention time as 1cc, was apparently unaffected by the pyrolysis conditions used.

e. This redistilled α-phellandrene contained 5 major contaminants, none of which appeared to be affected by pyrolysis up to 450°.

diene (5)[5], which can arise only by a series of reactions involving the triene (2), becomes significant at 360° and the ratio 5/(3+4) rises from 20% at 360° to 50% at 500° suggesting that the activation energy (E_a) for 2 → 5 is greater than that for 1cc or 1ct → 3, but that 4 and 5 are of comparable stability. The appearance of 5 only at *ca.*330° might be taken to indicate the absence of [1,7]-H-shifts below this temperature were it not for the interconversion of 1cc and 1ct.

While 1ct can yield only one [1,7]-H-shifted product (2), 1cc can also give 6cc, which is one of the initial photoproducts[11] formed in the irradiation[12] of α-phellandrene (7). On low temperature pyrolysis of a mixture of trienes (6) the only isomer to be affected is 6cc, which cleanly gives 1cc (see Table). At higher temperatures 6ct is decomposed, giving 7 which can be progressively isomerized, probably by a [1,5]-H shift, to α-terpinene (8).

Acknowledgment. We thank the National Science Council for support.

References.

1. C.W. Spangler and D.L. Boles, J.Org.Chem., 1972, 37, 1020.
2. W. von E. Doering and G.H. Beasley, Tetrahedron, 1973, 29, 2231.
3. P. Courtot and R. Rumin, Bull.Soc.Chim.Fr., 1972, 4238.
4. K.W. Egger and T.Ll. James, Trans.Faraday Soc., 1970, 66, 410.
5. E.D. Parker and L.A. Goldblatt, J.Amer.Chem.Soc., 1950, 72, 2151.
6. K.W. Egger, Helv.Chim.Acta, 1968, 51, 422.
7. A. Verloop, A.L. Koevoet and E. Havinga, Rec.Trav.chim., 1957, 76, 689
8. (a) C.J. Gaasbeek, H. Hogeveen and H.C. Volger, Rec.Trav.chim., 1972, 91, 821; (b) G. Frater, Helv.Chim.Acta, 1974, 57, 2446.
9. (a) E.N. Marvel, G. Caple and B. Schatz, Tetrahedron Letters, 1965, 385; (b) H. Heimgartner, H-J. Hansen and H. Schmid, Helv.Chim.Acta, 1972, 55, 1385.
10. K.J. Crowley, J.Org.Chem., 1968, 33, 3679.
11. J.E. Baldwin and S.M. Krueger, J.Amer.Chem.Soc., 1969, 91, 6444.
12. K.J. Crowley, K.L. Erickson, A. Eckell and J. Meinwald, J.Chem.Soc. Perkin I, 1973, 2671.