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THE THERMAL REARRANGEMENT OF 5-METHYL-1,2,4-HEXATRIENE

A FACILE 1,5-HYDROGEN MIGRATION

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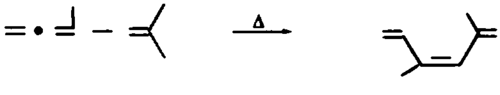
Abstract—The vinylallene 5-methyl-1,2,4-hexatriene (1) has been shown to rearrange rapidly at about 100° to *cis*-2-methyl-1,3,5-hexatriene (2). The activation energy for the reaction was found to be 24·6 kcal mole^{-1}, one of the lowest values recorded for a 1,5-hydrogen shift. The effect of the allenic grouping on the transition state is discussed.

THERMAL uncatalyzed intramolecular rearrangements of allenes containing an additional allenic linkage or a double bond in the molecule have been studied by several groups.[1] Some of these reactions were quite selective and afforded in excellent yields various interesting olefins, difficult to obtain otherwise. In the cases where the unsaturated bonds are separated by two C atoms, a Cope-type rearrangement seems to be the best mechanistic explanation[1f] of the results. Recently[1e] a vinyl allene *viz.* 2-methyl-1,3,4-pentatriene was shown to equilibrate in the gas phase at 350–450° to a mixture containing an equal amount of starting material and 1-methyl-3-methylenecyclobutene. The conversion of a methylenecyclobutene to the corresponding vinylallene under similar conditions had previously been reported[2] but the reverse reaction was not mentioned. On the other hand, the present study shows that the thermal rearrangement of the vinylallene 5-methyl-1,2,4-hexatriene (1) yields exclusively *cis*-2-methyl-1,3,5-hexatriene (2) as the primary product and no methylenecyclobutene derivative.

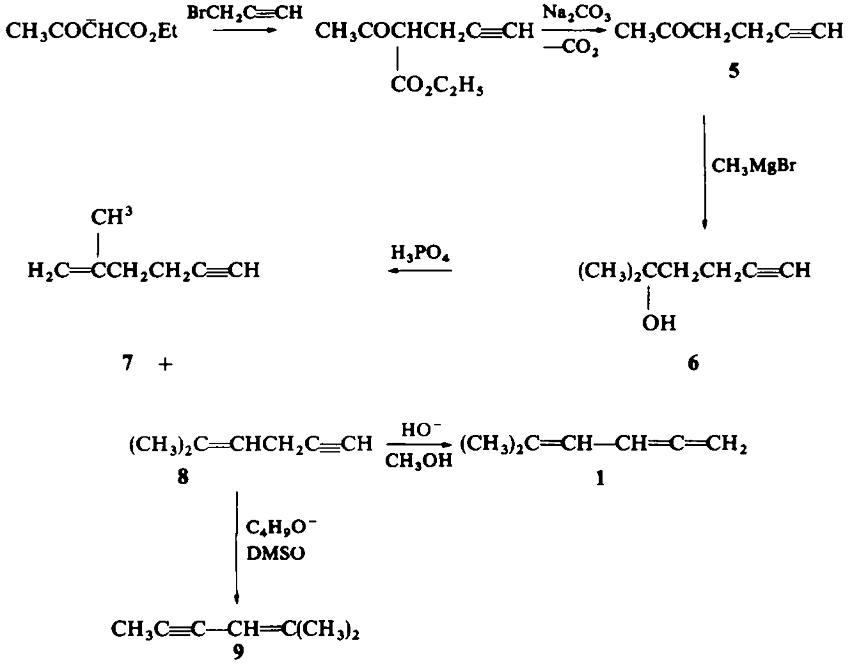
We had observed[3] that the reaction of 1,1-dibromo-2-isobutentyl-2-methylcyclopropane with methyllithium yielded besides 2,5,5-trimethylcyclopentadiene a small amount of *cis*-2,4-dimethyl-1,3,5-hexatriene (3). It was concluded that 3 was formed from the vinyl allene 3,5-dimethyl-1,2,4-hexatriene (4) by a thermally induced 1,5-hydrogen shift taking place during distillation of the products. This



4 3

would, however, imply that rearrangement had to take place at a fairly fast rate at about 120°, an unusually low temperature for 1,5-hydrogen shift to occur in a non-cyclic system; the rearrangement of 4-methyl-1,3-pentadiene to *cis*-2-methyl-1,3-pentadiene required a temperature of about 400°.[4] This prompted the study of a model compound under thermal conditions, for which compound (1) was chosen because the *gem*-dimethyl arrangement would preclude any stereochemical problems; a *cis* configuration about the double bond is a condition for rearrangement. Reactions leading to the allene are outlined in Scheme 1. The ketone **5** was obtained from sodium acetoacetate and propargyl bromide followed by hydrolysis and decarboxylation.[5] Methylmagnesium bromide was added to the ketone to give the carbinol **6** in 51% yield.[6] Dehydration with orthophosphoric acid afforded a mixture of about equal amounts of the hydrocarbons **7** and **8** in 90% yield. These were successfully separated on an efficient spinning band column. The treatment of **6** under similar conditions has been claimed[6] to yield exclusively compound **8**, but the reported physical constants of the product are not in agreement with those of **8**. The higher boiling isomer **8** partially rearranged to the desired allene (**1**) with 5% methanolic potassium hydroxide. However, it was more convenient to treat the above isomer mixture under the same conditions and then separate the allene by fractionation; this resulted in a product consisting of 56·6% **7**, 7·0% **8** and 36·4% **1**. Further heating resulted only in lower yield and relatively less of the allene, probably due to secondary reactions. The use of potassium t-butoxide in dimethylsulfoxide resulted only in rearrangement, presumably *via* **1**, to the conjugated vinylacetylene **9**. The fairly unstable allene was characterized by infrared, ultraviolet and NMR spectra. It has recently been reported[7] as a product from the acetolysis of 2,2-dimethyl-3,4-pentadienyl *p*-bromobenzenesulfonate; the NMR data are in complete agreement with ours.

Scheme I



$CH_3CO\bar{C}HCO_2Et \xrightarrow{BrCH_2C\equiv CH} CH_3COCH(CO_2C_2H_5)CH_2C\equiv CH \xrightarrow[-CO_2]{Na_2CO_3} CH_3COCH_2CH_2C\equiv CH$ **5**

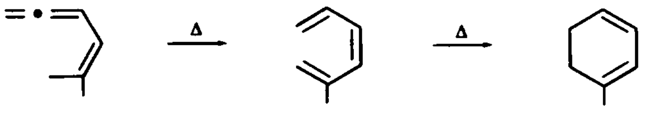
5 $\xrightarrow{CH_3MgBr} (CH_3)_2C(OH)CH_2CH_2C\equiv CH$ **6**

6 $\xrightarrow{H_3PO_4} H_2C{=}C(CH^3)CH_2CH_2C\equiv CH$ **7** + $(CH_3)_2C{=}CHCH_2C\equiv CH$ **8**

8 $\xrightarrow[CH_3OH]{HO^-} (CH_3)_2C{=}CH{-}CH{=}C{=}CH_2$ **1**

8 $\xrightarrow[DMSO]{C_4H_9O^-} CH_3C\equiv C{-}CH{=}C(CH_3)_2$ **9**

When the allene was passed through a tube packed with Pyrex wool and kept at 135°, 10% conversion to an isomeric compound took place. This was separated by preparative GLC and identified as *cis*-2-methyl-1,3,5-hexatriene (**2**) on the basis of spectroscopic evidence.* At 185° a second compound was present in the product together with **2** and unreacted **1** and at 330° this became the exclusive product, shown to be 1-methyl-1,3-cyclohexadiene[9] (**10**).



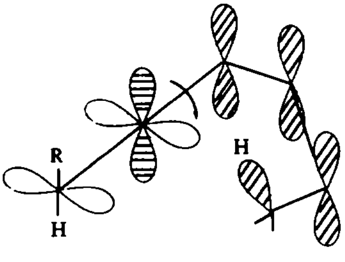
1 **2** **10**

The formation of **2** was measured kinetically in the gas phase.† It is a clean first order process, $k = 2{\cdot}73 \,.\, 10^{-4}$ at 113·4° with an activation energy, $E_a = 24{\cdot}6$ kcal/mole. This is the lowest activation energy of any known thermal 1,5-hydrogen transfer in an open-chain system, and in Table 1 activation energies of some established rearrangements of this type are compared. The quite similar rearrangement of *cis*-2-methyl-1,3-pentadiene (**11**) has roughly 8 kcal higher activation energy, and the reason for this substantial difference is not at all clear.

TABLE 1. THERMAL 1,5-HYDROGEN TRANSFER REACTIONS

Rearrangement			E_a Kcal/mole
5-Methylcyclopentadiene	→	1-methylcyclopentadiene	20·4[10]
Cycloheptatriene	→	cycloheptatriene	31[11]
1,3,6-Cyclooctatriene	→	1,3,5-cyclooctatriene	27·3[12]
cis-2-Methyl-1,3-pentadiene	→	4-methyl-1,3-pentadiene	32·8[13]
1	→	**2**	24·6

The answer must be found in the effect of the allenic linkage on the transition state, since this is the only significant structural difference between **1** and **11**. If the transition state resembles starting material, the unique symmetry of the allenic bond precludes participation of the terminal allenic π-electrons (white lobes in **12**). On the other hand, in a transition state resembling the product, which has a more extended conjugation than starting material, a stabilizing contribution of the said π-electrons would be expected; with other words, the stabilizing effect would be determined by the degree of twist, in the transition state, of the bond indicated below (**12**).



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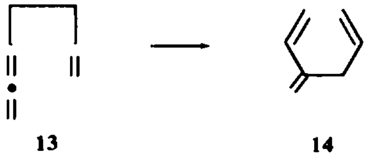
* The *trans* isomer has been prepared.[8]

† We want to thank Dr. R. Srinivasan for these measurements.

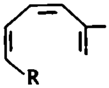
Furthermore, a striking difference between the thermal reactions of **1** and **11** is that hydrogen migrates to carbons of different electronegativity, sp and sp^2, respectively. This could also contribute to a lower activation energy in the case of the allene. A vinylic CH bond is about 6–10 kcal stronger than a normal CH bond.[14] If one assumes that in the transition state the migrating hydrogen is halfway between the 1,5 carbons this difference could result in as much as 3–5 kcal lowering of the activation energy. It is interesting that the activation energy of the related rearrangement, **13** to **14**, was found to be 28·74 kcal/mole about 4 kcal lower than that for the related rearrangement of 3-methyl-1,5-hexadiene.[1f] Similar arguments to those presented above could also apply to this reaction.



13 **14**

The conversion **2** → **10** represents another example of a well-established thermal rearrangement.[15] It is generally a very facile reaction, and it is not at all surprising that **10** was present in the product from passing the allene **1** through the tube at 185°.

A result of the hydrogen rearrangement is that the terminal allenic hydrogens of **1** has rotated 90° into the plane of the molecule. If one of these hydrogens is replaced by a substituent R, two isomers could be obtained depending on the direction of rotation. It would be of interest to see if theory predicts any stereochemistry in such a system. According to the Woodward–Hoffmann rules a concerted 1,5-sigmatropic hydrogen migration in a 1,3-diene is thermally allowed as a suprafacial process.[16] In the case of an allene like **12** two distinctly different modes of migration are available to the hydrogen. First, it can migrate to the double bond which is part of the conjugative system (shaded lobe of the central allenic carbon of **12**). This is not different from the case of an ordinary 1,3-diene and the rules predict no stereoselectivity e.g. equal amounts of the two possible isomers **15** and **16**. The other possibility is migration to the terminal allenic double bond (white lobe of the central allenic carbon in **12**). In this case an eight electron system is involved and using the criterion that only those processes having an odd number of suprafacial transformations are thermally allowed,* combinations can be depicted which make the formation of either **15** or **16** thermally allowed. Hence, theory does not predict stereoselectivity in these reactions whether six or eight electrons are involved. This certainly does not preclude the possibility of selectivity caused by simple steric hindrance.



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* The author wants to thank one of the referees for some most constructive comments with regard to this point.

EXPERIMENTAL

B.ps and m.ps are uncorrected. The IR spectra were obtained on a Beckman IR-5A and IR-10 spectrometer. The UV spectra were measured in n-heptane soln on a Cary Model 14 spectrometer. The NMR spectra were recorded on a Varian A-60 instrument with CCl_4 as solvent and TMS as internal standard. The chemical shifts are given in δ values. Analytical GLC was carried out on an 8 ft silicone column, when not otherwise stated.

5-*Hexyne-2-one* (5) was prepared according to the literature,[5] b.p. 60° (30 mm); n_D^{23} 1·4355.

2-*Methyl-5-hexyn-2-ol* (6) was obtained in 51% yield from 5 and MeMgBr,[6] b.p. 72° (25 mm) n_D^{25} 1·4435 (lit.[6] b.p. 67° (20 mm), n_D^{20} 1·4447).

2-*Methyl-1-hexen-5-yne* (7) *and* 2-*methyl-2-hexen-5-yne* (8). A mixture of 34·6 g (0·31 mole) of 6 and 5·2 g 85% orthophosphoric acid was heated at 150°. The hydrocarbon and water distilled off as formed yielding 26·3 g (90%) of a mixture of 7 and 8. GLC showed the presence of 51·4% 7 and 48·6% 8. These were effectively separated on a spinning band column;* 7, b.p. 102°; n_D^{25} 1·4288; ν_{max} 3300, 2100 ($C{\equiv}CH$), 1650, 880 cm^{-1} ($C{=}CH_2$); NMR: broad singlets 4·73 ($=CH_2$), 2·25 (CH_2) and complex absorption 1·88–1·70 (CH_3, $\equiv CH$) with peak area ratio 2:4:4, 8, b.p. 107°, n_D^{25} 1·4374; ν_{max} 3300, 2105 ($C{\equiv}CH$), 1675 cm^{-1} ($C{=}CH$); NMR multiplets 5·17 ($C{=}CH$), 2·82 (CH_2) and complex absorption in the 1·85–1·58 region ($\equiv CH$, CH_3) with area ratio of 1:2:7, respectively. Compound 8 has been reported,[6] b.p. 101°, n_D^{20} 1·4464, but the product cannot have been homogeneous.

5-*Methyl*-1,2,4-*hexatriene* (1). The above mixture, 26·1 g (0·31 mole) was added to a soln of 5 g KOH in 150 ml MeOH and heated under reflux for 24 hr. GLC analysis showed that most of compound 8 had rearranged to the allene; further heating reduced the amount of 1, probably due to secondary reactions. The soln was poured into 1 l. water, the organic phase separated, and the aqueous phase extracted with ether. The combined organic phase and extract was washed with water and dried ($MgSO_4$). GLC analysis showed the presence of 56·4% (7), 7·0% (8) and 36·6% 1, besides ether. The ether was distilled through a column, and the residue short path distilled under vacuum giving 24·3 g (93%) of the isomer mixture. The allene (1) was separated by fractional distillation through a spinning band column,* b.p. 55° (60 mm); n_D^{22} 1·4997; ν_{max} 1935, 840 ($C{=}C{=}CH_2$), 870 cm^{-1} ($C{=}CH$); λ_{max} 2305 (ε 25700); NMR weakly split (<1 Hz) singlets at 1·70 and 1·77 (CH_3), a secondary split (~1 Hz) doublet 4·78 ($=C{=}CH_2$) and complex absorption between 6·11–5·35 (vinyl H); the compound is unstable turning rapidly yellow in air. It can be kept unchanged for a long period of time at −78°, at which temp it is a solid. Leaving a soln of 8 in DMSO with catalytic amounts of t-BuOK at room temp overnight resulted in formation of 9; NMR multiplet 5·18 ($=CH$), doublet, $J = 2{\cdot}5$ Hz, 1·93 ($\equiv CCH_3$), singlet 1·83 ($=C{-}CH_3$) and multiplet, $J < 1$ Hz 1·78 ($=C{-}CH_3$); the area ratio is 1:3:3:3.

1-*Methyl*-1,3-*cyclohexadiene* (10) was obtained in quantitative yield by passing 1 through the tube at 330° (15 mm); GLC showed >98% purity; n_D^{25} 1·4749; λ_{max} 262 mμ (ε 6800); NMR complex absorption 5·35–6·0 ($=CH$) and broad singlets 2·09 (CH_2), 1·78 (CH_3) with peak area ratio of ~3:4:3; (lit.[9] n_D^{25} 1·4813; λ_{max} 263 mμ (log ε 2·64)). *Maleic anhydride adduct* was formed in the usual way, m.p. 59–60° from benzene (lit.[9] m.p. 61°).

cis-2-*Methyl*-1,3,5-*hexatriene* (2) was separated by preparative GLC using an Apiazone L column; ν_{max} 995, 895 ($-CH{=}CH_2$), 780 cm^{-1} (*cis*-$CH{=}CH$); λ_{max} 249 (29000), 259 (35000), 269 mμ (28300); the NMR spectrum shows complex vinylic absorption in 2·7–5·2 region and a weakly coupled triplet (J ~ 1 Hz) at 2·18 due to the Me group. (λ_{max} (iso-octane) for *trans* 2,[17] 247·5 (25700), 256·5 (35800) 267 mμ (28500).) The compound did not react with maleic anhydride in benzene up to 80°.

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