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FORMATION OF LINEAR TRIQUINANES BY SERIAL HOMOLYTIC CYCLISATION

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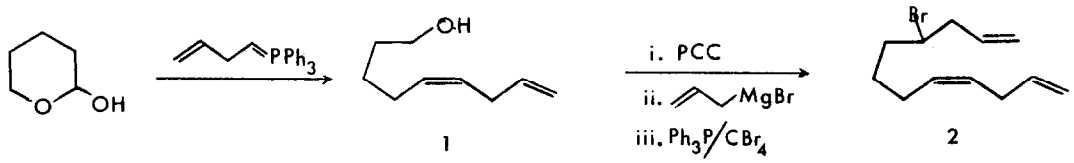
Summary: Treatment of the trienyl bromide (2) with tributylgermane affords the two stereoisomers of 4-methyl-cis,anti,cis-tricyclo[6,3,0,$0^{2,6}$]undecane (9) (27%) and related tricyclic compounds by processes involving three consecutive radical ring closures

Ring formation by intramolecular homolytic addition in suitably constituted alkenyl radicals[1] usually conforms to guidelines based on stereo-electronic considerations,[2] and often proceeds with much higher regio- and stereo-selectivity than would have been expected from simple thermochemical criteria. Consequently, even reactions involving two consecutive ring closures sometimes give only one or two major products[3] and are thus of potential utility for synthesis. We now describe the formation of compounds containing the linear triquinane system by three consecutive ring closures of the alkatrienyl radical (6).

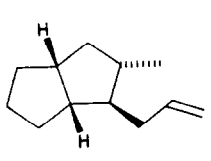
A suitable radical precursor (2) was easily prepared from readily available starting materials as shown in Scheme 1. A key step was the Wittig reaction which afforded the alcohol (1) as its Z isomer, the NMR spectra of which confirmed the assignment of configuration. It was important to work with the pure Z isomer of the bromide (2) because of indications[4] that the stereochemistry of ring closure of radicals containing a 1,6-disubstituted hex-5-enyl system depends critically on the configuration of the double bond.



Scheme 1

Heating of the bromide (2) in benzene at 80° with tributylgermane[5] (0.02M) and a trace of radical initiator (azobisisobutyronitrile) for 20 hours gave a mixture shown by capillary GLC to contain eight products: A, 14%; B, 10%; C, 6%; D, 18%, E, 9%; F, 4%; G, 24%; and H, 12%. The mixture could not be completely separated into its components by chromatographic techniques, but careful preparative GLC gave three fractions suitable for examination by NMR spectroscopy.

Fraction I, containing compounds A, B and C, showed ^{13}C NMR resonances for one double bond (δ 115.2 and 137.7), two methyl carbons (δ 19.1 and 23.6) and numerous methylene and methine carbons. When the mixture was treated with bromine, A was destroyed. We conclude that A is a bicyclic compound with a pendant allyl group such as 3 or 4. If, as seems likely (see below), A is (3) or one of its stereoisomers, then both B and C must be saturated tricyclic compounds. That which contains the methyl group must be a stereoisomer of a linear triquinane (e.g. 13) while the other must be a stereoisomer of tricyclo[6,4,0,$0^{2,6}$]dodecane (e.g. 17).



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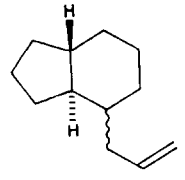

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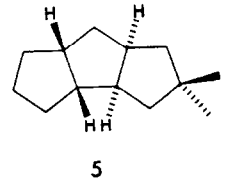

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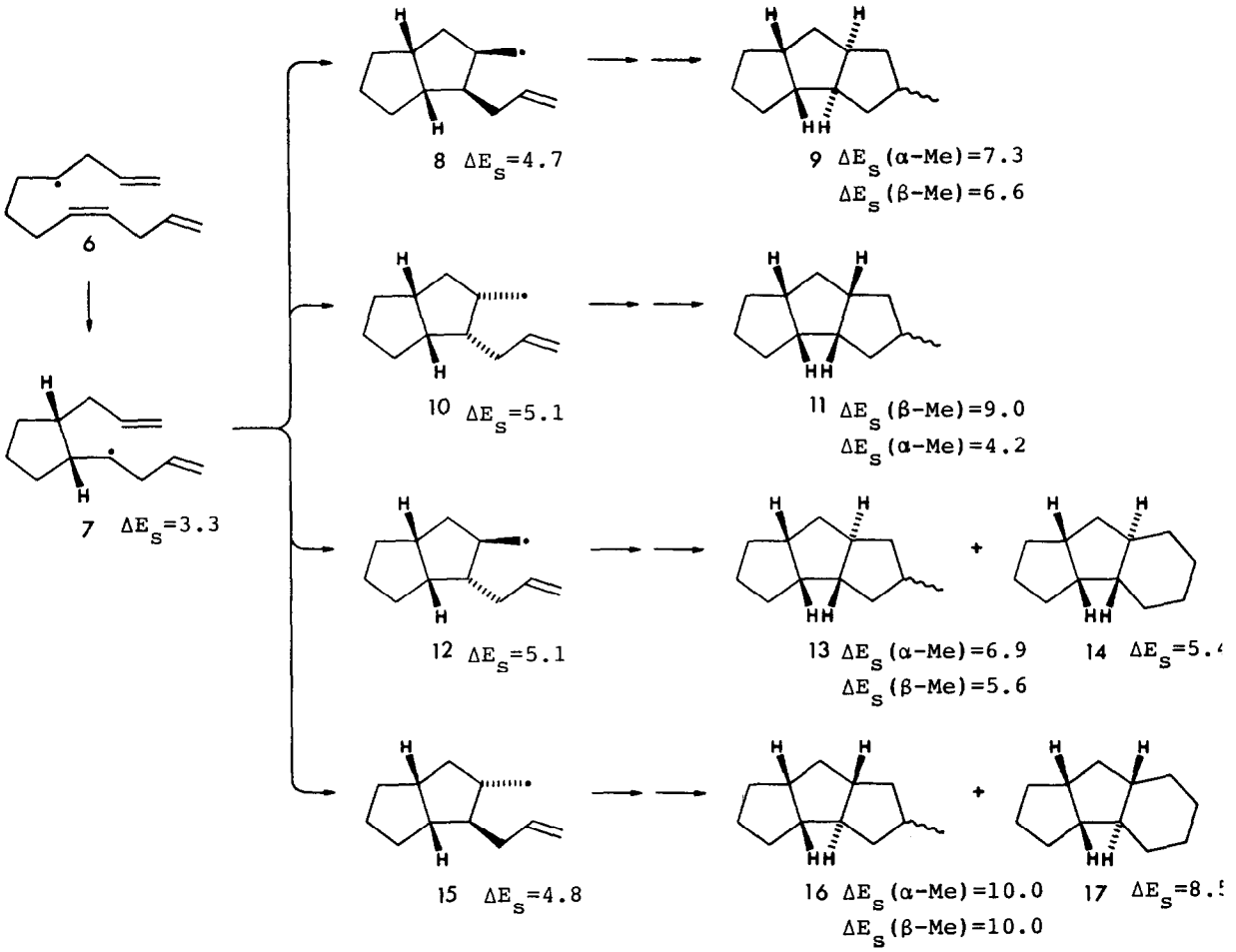
The second fraction contained compounds D and E. As resonances for two methyl carbons could be clearly discerned in the ^{13}C NMR spectrum, D and E must each be a methyl triquinane. The close correspondence of most of the ^{13}C NMR resonances (Table 1) with those for the known dimethyl compound (5)[6] strongly indicates that D and E have the structures 9 (β-Me) and 9 (α-Me) respectively. It is not possible to assign all of the resonances in Table 1. However, it seems reasonable to assign those which differ most between the reference and compounds D and E (i.e. at δ 48.1 and 49.0 in 5 and at about 42 ppm in the isomers of 9) to C-3 and C-5.

Table 1 ^{13}C NMR Data (δ, ppm) for Methyl Triquinanes

Compound	Methyl C		Methylene C						Methine C				
5[6]	28.1	29.9	25.8	32.0	33.0	39.8	48.1	49.0		44.0	44.2	50.9	52.1
D	20.2		25.8	32.3	33.5	40.1	42.2	43.3	36.8	40.1	45.2	51.9	52.3
E	20.3		25.9	32.3	33.7	40.6	41.9	42.7	33.3	40.6	45.4	51.5	52.4

Fraction III, containing compounds G and H, showed two distinct sets of ^{13}C resonances. The more intense set contained signals for 4 methine and 8 methylene carbons, but no methyl signal. Since no olefins could be detected we conclude that G, the major component



Scheme 2. Intermediates and products for serial cyclisation of the trienyl radical (7). Values of transition structure strain energies[9] (ΔE_S) are in kcal.mol^{-1}

of the mixture, is a tricyclododecane. The less intense set contained 5 methine, 6 methylene, and one methyl resonance. H, therefore, is a methyl-triquinane.

In view of the utility of MM2 force field calculations[7] for predicting the regio- and stereo-chemistry of simple radical ring closures,[8] we decided to apply this method to the present system. Relevant values of ΔE_S (transition structure strain energies)[9] are shown in Scheme 2. Important features of these data are: a) cis-ring closure is strongly favoured in the first step [ΔE_S(trans) = 4.9 kcal.mol^{-1}] and we conclude, therefore, that all of the products, including A, are formed via 7; b) in the second step, formation of 8 and 15 is slightly favoured; c) the sole olefin produced (A) must be derived from the radical (15) for which there is no low energy ring closure process available; d) the formation of only two compounds, (14) and (17), containing the tricyclo[6,4,0,$0^{2,6}$]dodecane nucleus appears to be

energetically feasible; e) the formation of 11(β-Me) and the two isomers of 16 appears to be energetically precluded and formation of 13(α-Me) is unlikely since a competing process of lower energy is available.

The MM2 calculations thus predict the formation of two tricyclo[6,4,0,$0^{2,6}$]dodecanes (14 and 17), and four triquinanes [11(α-Me), 13(β-Me), and the two isomers of 9], with the possibility of a fifth [13(α-Me)]. The experimental data indicate that the reaction affords two tricyclododecanes (B and G) and four triquinanes (C, D, E, and H); possibly F for which no spectral data were obtained is also a triquinane. Two major products, D and E, have been identified as the stereoisomers of the triquinane 9. In the light of the MM2 data it seems reasonable to tentatively identify B and G as 17 and 14, and C and H as 13(β-Me) and 11(α-Me) respectively. A, the sole unsaturated product, is probably the compound (3) arising from the only bicyclic intermediate (15) with no energetically favourable pathway available to it.

In conclusion, it appears that serial cyclisation of suitable polyolefinic radicals can afford moderately tractable mixtures of polycyclic products. Although in the present case, the assignment of structure and stereochemistry is reasonably secure only for two products (the isomers of 9) the method is of such simplicity as to warrent further examination.

References and Notes

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