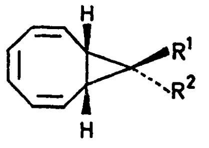
Product Characterization in the Thermal Bond-relocation of the *syn*- and *anti*-9-Methylbicyclo[6,1,0]nona-2,4,6-trienes

By A. G. ANASTASSIOU* and R. C. GRIFFITH

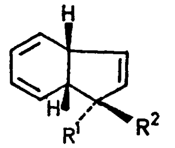
(*Department of Chemistry, Syracuse University, Syracuse, New York* 13210)

Summary *anti*-9-Methylbicyclo[6,1,0]nona-2,4,6-triene thermolyses overwhelmingly to a *cis*-8,9-dihydroindene skeleton while under similar conditions the *syn*-counterpart generates a mixture consisting of *ca.* 70% *cis*-fused and 30% *trans*-fused 8,9-dihydroindenes.

IN a recent re-examination of the title reaction[1] we established that the isomers shown in (**1a**) and (**1b**) display markedly different heat sensitivities,† *e.g.*, $k_{\mathrm{a}}/k_{\mathrm{s}}$ *ca.* 100 at 151°, and that, contrary to an earlier report,[2] these substances do not thermolyse to the same product mixture. We now formulate all hitherto uncharacterized thermolysis products and propose a rationale to account for the thermolytic differences between (**1a**) and (**1b**).



(1)



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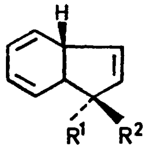

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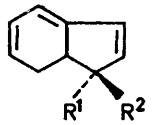

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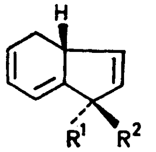
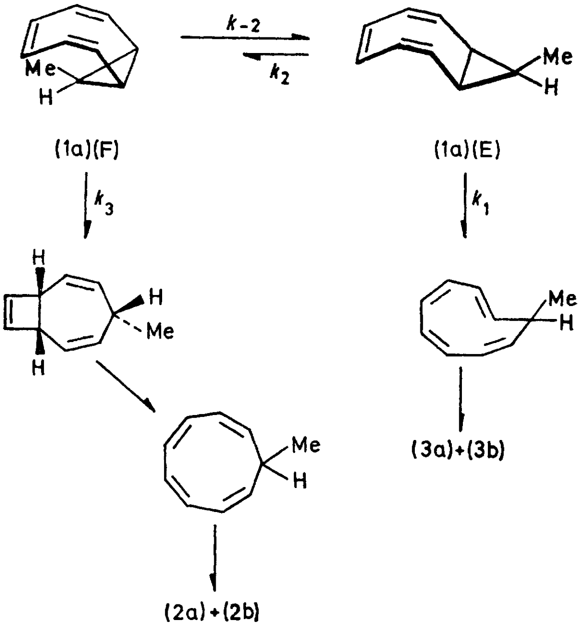


(5)

a; $R^1 = H$, $R^2 = Me$
b; $R^1 = Me$, $R^2 = H$



SCHEME

Thermolysis of the *syn*-isomer (**1a**) over a range of temperatures (110—199°) and for varying degrees of completion (17 to >90%) generates a mixture which invariably consists (g.l.c.) of *ca.* 68% of the *cis*-fused dihydroindenes (**2a**) and (**2b**) in a ratio of *ca.* 3·8 : 1. The composition (g.l.c.)

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† Professor P. v. R. Schleyer recently informed us of related, unpublished observations by Professor W. Grimme (Habilitationsschirift, Köln, 1968) on the relative reactivities of (**1a**) and (**1b**). These observations appear to have been misrepresented in a recent reference to Professor Grimme's work.

of the remaining 32% of the thermolysate is a function of both time and temperature, consisting of only two components (A) (35%) and (C) (65%), when generated after (**1a**) had been heated at 179° for 30 s, (*ca.* 17% reaction) and of four additional components; (B), (D), (E), and (F) [formed at the expense of (A) and (C)], when produced either on more prolonged heating (5 min) at the same temperature or on brief heating (30 s) at a higher temperature (199°).

These findings clearly require that of the six new substances detected only (A) and (C) be primary thermolysis products. Indeed, heating of (C) (collected by g.l.c.) at 179° for 5 min (*ca.* 58% reaction) generated a 1·5 : 1 mixture of (E) and (B) respectively while under the same conditions thermolysis of pure (A) (collected by g.l.c.) led to a 6·6 : 1 mixture of (D) and (F) respectively (75% reaction).

Components A—E were collected by g.l.c. Spectral data coupled with the fact that each compound oxidizes to 1-methylindene[3] when exposed to air‡ are consistent with the following formulation:§ (A) = (**3b**), (C) = (**3a**), (B) = (**5a**), (D) = (**4b**), and (E) = (**4a**). Further, in light of these assignments we tentatively formulate (F)¶ as (**5b**). The four secondary products thus appear to arise from the primary pair through one of two symmetry controlled 1,5 hydrogen shifts.

In sharp contrast to (**1a**) the *anti* analogue (**1b**) thermolyses to a mixture which consists almost exclusively (>90%) of the *cis*-fused pair (**2a**) and (**2b**) in a ratio of 3·7 : 1.

The distribution of products obtained from the thermolysis of (**1a**) and (**1b**) is best accommodated in terms of the various transformations shown in the Scheme. The central feature of this Scheme is of course that the stereochemical outcome of the rearrangement is a particularly sensitive function of reactant conformation and that thermolysis from the folded arrangement (**1a**) (F) is by far the preferred course, *i.e.*, $k_3 \gg k_1$. Further, within the frame of this Scheme the ratio of *cis*-fused to *trans*-fused 8,9-dihydroindenes suggests that k_1/k_{-2} = *ca.* 3/7. It is also noted in this connection that the *anti*-isomer (**1b**), having ready steric access to a folded arrangement requires less energy ($\Delta\Delta F^{\ddagger}$ *ca.* 4 kcal/mol)[1] for thermal activation.

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‡ The primary pair (A) and (C) undergoes this oxidation more rapidly than the secondary products.

§ The spectral characteristics of these five products are entirely analogous to those of their dialkyl counterparts (S. W. Staley and T. J. Henry, *J. Amer. Chem. Soc.*, 1969, **91**, 1239, 7787) which were also used as models for specific assignment of the methyl disposition in (A) and (C). We thank Professor S. W. Staley for detailed spectral information on the dialkyl system.

¶ The trace amounts in which (F) is produced coupled with its partial coincidence with (C) in the chromatographs precluded its isolation.

[1] A. G. Anastassiou and R. C. Griffith, *Chem. Comm.*, 1971, 1301.
[2] P. Radlick and W. Fenical, *J. Amer. Chem. Soc.*, 1969, **91**, 1560.
[3] H. Christol and F. Plenat, *Bull. Soc. chim. France*, 1962, 1325.