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

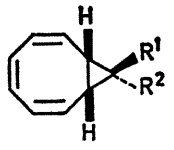
By A. G. ANASTASSIOU* and R. C. GRIFFITH

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

Summary The title compounds were found to thermolyse at widely different rates and thermolysis of the *syn*-isomer was found not to yield the product distribution reported previously.

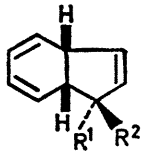
WE recently stressed[1] the importance of conformational factors in the thermal reorganization of the general system shown in the triene (**1**) and remarked that when given a choice such a substance appears to favour thermolysis by way of a folded arrangement (**3**) to produce, eventually, a *cis*-dihydroindene (**2**). Conversely, thermal rearrangement through an extended conformation (**4**), which is no doubt the case with the sterically constrained 9,9-dialkyl derivatives of (**1**),[2] occurs less readily and generates a *trans*-

fused dihydroindene skeleton as the final product. This scheme accommodates the literature with the single exception of a recent claim[3] that the title compounds produce the same product mixture on heating. Owing to this apparent inconsistency[4] we re-examined the thermolytic behaviour of compounds (**1b**) and (**1c**) and we report certain key features of this rearrangement which appear to have escaped attention in the previous study.[3]



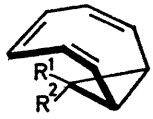
(1)

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



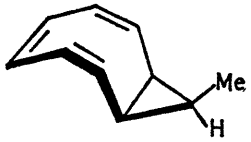
(2)

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



(3)

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



(4)

Compounds (**1b**) and (**1c**) thermolyse with widely different rates. Whereas the *anti*-isomer (**1c**) rearranges reasonably quickly when heated at 76° ($t_{\frac{1}{2}}$ *ca.* 195 min) the *syn*-counterpart (**1b**) is practically thermally inert at this temperature. At 151° the rearrangement of the *syn*-isomer has a $\Delta G^{\ddagger}$ term *ca.* 4 kcal mol^{-1} greater than that of the *anti*-analogue, *i.e.* k_a/k_s *ca.* 100. This pronounced difference in the energy necessary for the thermal activation of these compounds is indicative of a distinct preference for thermal bond-relocation by way of a folded arrangement which is readily accessible only to the *anti*-isomer, *i.e.* conformations (**3a**). Hence, the higher temperature required to activate the *syn*-isomer probably reflects the extra energy necessary either to force this substance into the sterically unfavourable but highly reactive folded arrangement shown in conformation (**3b**), or to permit its thermolysis from the sterically more stable but less labile extended form shown in conformation (**4**), or perhaps to activate a combination of both processes. The situation is further complicated by the possibility of a *syn*- to *anti*-isomerization during thermolysis. The influence of conformation on the energetics of the thermolysis of compounds (**1b**) and (**1c**) is evident from a comparison of the activation data in the Table which reveal a close similarity between the *anti*-isomer and the parent hydrocarbon (**1a**) on the one hand and between the *syn*-isomer and the 9,9-dimethyl analogue (**1d**; $R^1 = R^2 = Me_3$) on the other.

TABLE

Thermal activation data at 151° *relating to compound* (**1**).

Substrate	$\Delta G^{\ddagger}$/kcal mol^{-1}	k/s^{-1}
(**1a**)[a]	28	$3{\cdot}2 \times 10^{-2}$
(**1c**)[b]	27·4	$6{\cdot}5 \times 10^{-2}$
(**1b**)[c]	31	$5{\cdot}9 \times 10^{-4}$
(**1d**) ($R^1 = R^2 = Me$)[b] ..	32	$1{\cdot}8 \times 10^{-4}$

[a] Data obtained by monitoring the thermal rearrangement by n.m.r. spectroscopy at four different temperatures in the range 81°—101° ($\Delta H^{\ddagger}$ = 26 kcal mol^{-1}; $\Delta S^{\ddagger} = -5$ e.u.)[1] [b] Values obtained as in *a* at four different temperatures in the range 56°—86° ($\Delta H^{\ddagger}$ = 27·3 ± 0·6 kcal mol^{-1}; $\Delta S^{\ddagger} = -0{\cdot}3 \pm 1{\cdot}7$ e.u.) [c] Constants evaluated by monitoring the loss of reactant by n.m.r. at 151°. [d] Values calculated from half-life data recorded elsewhere.[2]

The data prompted us to re-examine the thermolytic behaviour of compounds (**1b**) and (**1c**) in terms of product distribution as well. This repetition was especially important for the isomer (**1b**) which should not thermolyse exclusively to a *cis*-dihydroindene skeleton [(**2b**) + (**2c**)] as previously claimed.[3] To this end, pure samples of compound (**1b**) were heated in evacuated sealed Pyrex tubes at several temperatures from 110—199°, and to varying degrees of partial reaction (17% to >90%), and the resulting thermolysates were immediately analysed by g.l.c.

Compounds (**2b**) and (**2c**) invariably constitute only 70% of the product mixture (not 95% as previously indicated[3]),† the remaining 30% consisting of four components only, two of which are primary products.‡ Thus, there are two energetically comparable competing processes in the thermolysis of compound (**1b**). The ready oxidative conversion of the four components into 1-methylindene indicates that they are probably all [4,3,0] bicyclics. The two primary products may be the *trans*-fused counterparts of compounds (**2b**) and (**2c**).

Our preliminary findings on the thermolysis of the *anti*-isomer (**1c**) appear to confirm the earlier report[3] that the thermolysate is overwhelmingly rich in compounds (**2b**) and (**2c**). The *anti*-isomer employed in the present work was conveniently prepared by the direct photolysis of the *syn*-counterpart, a stereoisomerization which also obtained

† This discrepancy is not due to dissimilarity in reaction conditions since the two results remained discordant when the previously reported procedure was reproduced. Rather, it is possible that in the earlier work the product mixture became exposed to the atmosphere and the resulting 1-methylindene was not detected, as the thermolysate is quite sensitive to air.

‡ Control experiments established that (**2a**) and (**2b**) are not responsible for the formation of the remaining components.

in the case of the ethoxycarbonyl and hydroxymethyl analogue and which further supports our earlier suggestion[5] that conformation in these systems plays an important role in excited state processes as well.

We thank the National Science Foundation for support.

(*Received, July 5th,* 1971; *Com.* 1121.)

[1] A. G. Anastassiou and R. C. Griffith, *J. Amer. Chem. Soc.*, 1971, **93**, 3083.
[2] S. W. Staley and T. J. Henry, *J. Amer. Chem. Soc.*, 1969, **91**, 1239; 7787.
[3] P. Radlick and W. Fenical, *J. Amer. Chem. Soc.*, 1969, **91**, 1560.
[4] The discrepancy between the thermolytic behaviour of the title compounds and that of their dialkyl analogues was recognized in a recent review, J. M. Brown, *Annual Reports*, 1969, **66**, 377.
[5] A. G. Anastassiou and E. Yakali, *J. Amer. Chem. Soc.*, 1971, **93**, 3803.