9-(7-Cycloheptatrienyl)-*cis,cis,cis,cis*-cyclonona-1,3,5,7-tetraene; Synthesis and Bond-relocation

By A. G. Anastassiou,* (Miss) E. Reichmanis, and R. C. Griffith
(Department of Chemistry, Syracuse University, Syracuse, New York 13210)

Summary The title substance was synthesized and was found to respond stereospecifically under the influence of heat and light.

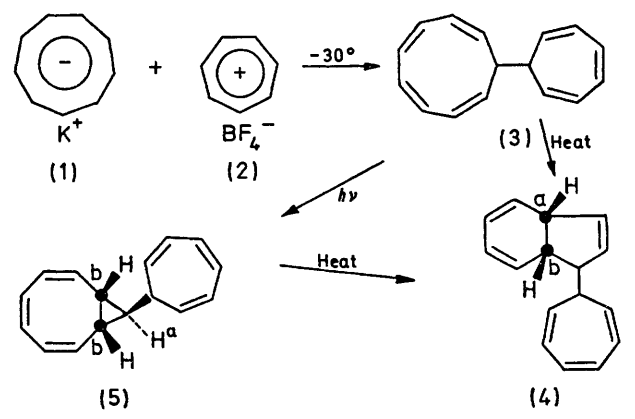
The mechanistic details defining the general C_9H_9R energy surface have attracted considerable attention in recent years.[1] We now record the synthesis and thermal and photochemical valence isomerization of the novel, sterically demanding, $C_{16}H_{16}$ member of this family (**3**).

Substance (**3**) was prepared by low-temperature (*ca.* $-30°$) neutralization of (**1**) with (**2**) in THF[2] and was isolated in pure form† (*ca.* 30%) on column chromatography (Al_2O_3) at *ca.* $-15°$. It is thermally labile and at ambient temperature rearranges readily [k (21·9°) $2{\cdot}9 \times 10^{-4}$ s^{-1}, $\Delta G^{\ddagger}$ (21·9°) 22·0 kcal/mol] and cleanly to (**4**),† the *cis*-fusion of the bicyclic C_9 portion of this product being deduced chiefly from the value of J_{ab} (12 Hz). The sterically demanding C_7 group present in (**3**) effectively reduces the thermal stability of the attached C_9 monocycle relative to that of its unsubstituted parent (cyclononatetraene)[3] by a rate factor of *ca.* 4 at 21·9°.

Direct irradiation of (**3**) (Pyrex-filtered; *ca.* $-15°$; in ether; *ca.* 0·75 h) with a Hanovia 450-W lamp, leads, cleanly and quantitatively, to (**5**),† m.p. 50—50·5°, which was

---

† This substance was subjected to full spectral characterization.



assigned an *anti* C_7 substituent on the basis of (i) the value of J_{ab} (5 Hz) and (ii) the appearance of the H^a resonance at an appropriately high field (τ 9·24). The stereospecificity of this process may be attributed to the conformational factors already advanced to account for the analogous cyclization of 9-chlorocyclononatetranene,[4] *i.e.*, excited state electrocyclization of (**3**) strictly to 'folded' (**5**) which in turn is sterically capable of sustaining *anti-* but not *syn*-substitution.

Finally, thermolysis of (**5**) produces (**4**) (i.r., n.m.r.) with a half-life, at 76·8°, of 240 min. We note that the activation energy associated with this process ($\Delta G^{\ddagger}$ 27·5 kcal/mol) is essentially identical with those controlling the analogous transformations of *cis*-bicyclo[6,1,0]nona-2,4,6-tetraene [$\Delta G^{\ddagger}$ (76·8°) 27·7 kcal/mol][5] and its *anti*-9-methyl counterpart [$\Delta G^{\ddagger}$ (76·8°) 27·4 kcal/mol][6] in full support of the original proposal[5] that steric access by a *cis*-bicyclo[6,1,0]-nona-2,4,6-triene to a 'folded' conformation is a strict prerequisite for ready thermolysis to a *cis*-8,9-dihydroindene skeleton.

We are now investigating in particular the possible generation of fulvalene-like structures on dehydrogenation of the connecting link in the $C_{16}H_{16}$ substances described herein.

We thank the National Science Foundation for support, and also Mrs. E. Yakali for the determination of several n.m.r. spectra.

(*Received*, *5th May* 1972; *Com.* 754.)

---

[1] For a comprehensive review of the subject see: S. W. Staley, *Intra Science Chem. Rept.*, 1971, **5**, No. 2, 149; see also A. G. Anastassiou and R. C. Griffith, *J. C. S. Chem. Comm.*, 1972, 399.

[2] The general synthetic procedures described here has precedent: M. E. Volpin, I. S. Akhrem, and D. N. Kursakov, *Khim. Nauk. Prom.*, 1957, **2**, 656; see also: W. v. E. Doering and H. Krauch, *Angew. Chem.*, 1956, **68**, 661.

[3] The rate constant associated with the thermal conversion of *cis,cis,cis*, *cis*-cyclononatetraene into *cis*-8,9-dihydroindene at 21·9° was estimated from the activation data recorded by G. Boche, H. Bohme, and D. Martens, *Angew. Chem.*, 1969, **81**, 565.

[4] A. G. Anastassiou and E. Yakali, *J. Amer. Chem. Soc.*, 1971, **93**, 3803.

[5] A. G. Anastassiou and R. C. Griffith, *J. Amer. Chem. Soc.*, 1971, **93**, 3083.

[6] A. G. Anastassiou and R. C. Griffith, *Chem. Comm.*, 1971, 1301.