

THERMAL BOND-RELOCATION OF THE STEREOISOMERIC  
9-CYANOBICYCLO[6.1.0]NONA-2,4,6-TRIENES

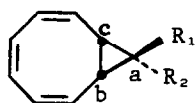
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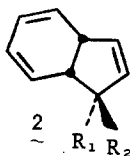
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RECENT mechanistic work with parent cis-bicyclo[6.1.0]nona-2,4,6-triene (1a)<sup>2</sup> and various 9-alkyl<sup>3</sup> and 9,9-dialkyl<sup>4</sup> derivatives has established the existence of strict conformational control whereby thermolysis to a cis-8,9-dihydroindene (2) originates from "folded" 1 and is associated with a  $\Delta G^\ddagger$  term of ca. 27.5 kcal/mole, while rearrangement to a trans-8,9-dihydroindene results from "extended" 1 and requires  $\Delta G^\ddagger \sim 32$  kcal/mole for thermal activation. Sharply contrasting their hydrocarbon relatives nitriles 1 (e,f,g) have recently been shown to thermolyze into [4.2.1] frames<sup>5</sup>, i.e., to undergo peripheral-bond (a-b) rather than cross-link (b-c) scission, and to require the input of significantly more thermal energy ( $\Delta G^\ddagger = 36.2$  kcal/mole for 1f and 35.6 kcal/mole for 1g)<sup>5b</sup>. Obviously then, the presence of a cyano substituent substantially strengthens (>3 kcal/mole) the cross-link of the "extended" form to which disubstituted nitriles 1 (e,f,g) are doubtlessly constrained.

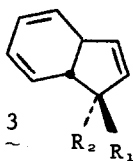
In an attempt to integrate the seemingly anomalous behavior of these cyano-carbons into the operational picture developed earlier for the hydrocarbons, we resolved to examine a 9-cyano variant with access to the "folded" geometry necessary for scission of the cross-link along the lower-energy path, i.e., that associated with  $\Delta G^\ddagger \sim 27.5$  kcal/mole in the hydrocarbons. The rationale here being of course that such a molecule may find it energetically beneficial to thermolyze with cross-link rupture in spite of added strength introduced into this bond by the nitrile function.



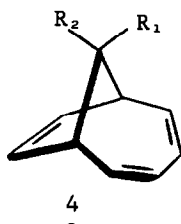
1



2



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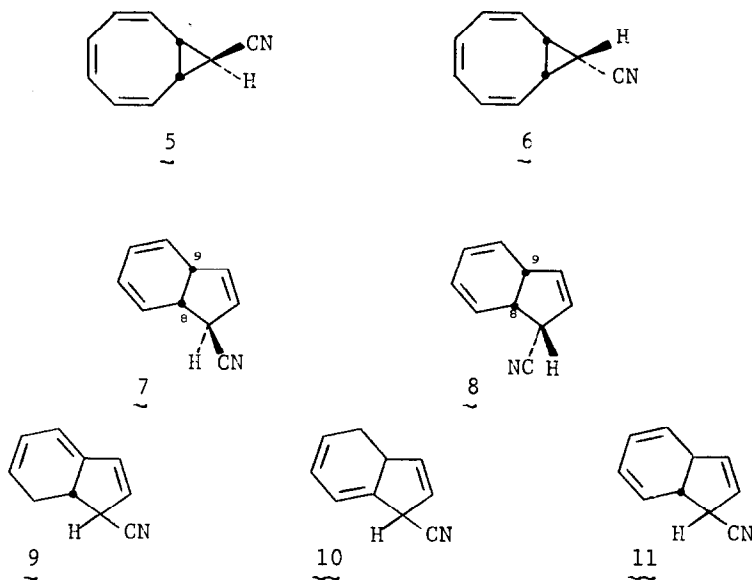


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a; R<sub>1</sub> = R<sub>2</sub> = Hb; R<sub>1</sub> = H; R<sub>2</sub> = alkylc; R<sub>1</sub> = alkyl; R<sub>2</sub> = Hd; R<sub>1</sub>, R<sub>2</sub> = alkyle; R<sub>1</sub> = R<sub>2</sub> = CNf; R<sub>1</sub> = CN; R<sub>2</sub> = Meg; R<sub>1</sub> = Me; R<sub>2</sub> = CN

To this end, we synthesized the 9-cyano isomers shown in 5 [mp. 89.5-90.5°;  $\nu_{\text{CN}}$  (KBr) 2210  $\text{cm}^{-1}$ ,  $\lambda_{\text{max}}$  (C<sub>6</sub>H<sub>14</sub>) 242.5 nm ( $\epsilon$  4700); nmr (60 MHz; C<sub>6</sub>D<sub>6</sub>)  $\tau$  4.1-4.2 (6H-m), 8.38 (2H-d,  $J = 5.5$  Hz), 9.57 (1H-t,  $J = 5.5$  Hz); m/e 143 (98%; P<sup>+</sup>)] and 6 [ $\nu_{\text{CN}}$  (KBr) 2210  $\text{cm}^{-1}$ ,  $\lambda_{\text{max}}$  (C<sub>6</sub>H<sub>14</sub>) 242.5 nm ( $\epsilon$  3300); nmr (100 MHz; C<sub>6</sub>D<sub>6</sub>)  $\tau$  4.0-4.5 (6H-m), 8.88 (2H, A component of A<sub>2</sub>B pattern,  $J_{\text{AB}} = 8.7$  Hz)<sup>6</sup>, 9.03 (1 H, B component of A<sub>2</sub>B pattern,  $J_{\text{BA}} = 8.7$  Hz)<sup>6</sup>; m/e 143 (65%; P<sup>+</sup>)] on treatment of COT dianion with dibromoacetonitrile in tetrahydrofuran and examined their thermal response at 139°<sup>7</sup>. On exposure to this temperature for 2 hr., the anti isomer (5) undergoes 85% reaction with  $k_a = 3.37 \pm 0.13 \times 10^{-4} \text{sec}^{-1}$  ( $\Delta G^\ddagger = 30.9$  kcal/mole)<sup>8</sup> to yield a mixture consisting of 52% 7<sup>9</sup> [ $\nu_{\text{CN}}$  (neat) 2230  $\text{cm}^{-1}$ ,  $\lambda_{\text{max}}$  (C<sub>6</sub>H<sub>14</sub>) 210 nm ( $\epsilon$  1500), 251 (sh) (3300), 259.5 (4200), 268 (3900), 278 (sh) (2100); nmr (100 MHz; CDCl<sub>3</sub>)  $\tau$  4.02 (1H-m), 4.1-4.3 (4H-m), 4.50 (1H-m), 6.28 (1H-d, H<sub>9</sub>,  $J_{9,8} = 11.5$  Hz), 6.5-6.8 (2H-m, H<sub>1</sub> + H<sub>6</sub>); m/e 143 (96%; P<sup>+</sup>)], 24% 8<sup>9</sup> [ $\nu_{\text{CO}}$  (neat) 2230  $\text{cm}^{-1}$ ,  $\lambda_{\text{max}}$  (C<sub>6</sub>H<sub>14</sub>) 210 nm (sh) ( $\epsilon$  2100), 251.5 (sh) (3200), 260 (4100), 268.5 (3900), 278 (sh) (2300); nmr (100 MHz; CDCl<sub>3</sub>)  $\tau$  3.8-4.4 (5H-m), 4.46 (1H-m), 6.17 (1H-m, H<sub>1</sub>), 6.37 (1H-d, H<sub>9</sub>,  $J_{9,8} = 11.5$  Hz), 6.70 (1H-m, H<sub>6</sub>); m/e 143 (100%; P<sup>+</sup>)] and 19% 6 (ir, uv). Under the same conditions the syn counter part 6 is consumed only to the extent of 47% with  $k_s = 0.90 \pm 0.05 \times 10^{-4}$

sec.<sup>-1</sup> ( $\Delta G^\ddagger = 32.0$  kcal/mole) to produce 49% 7 (ir, uv), 25% 8 (ir, uv) and 24% 5 (ir, uv). In addition, trace amounts (5% or less) of two substances tentatively identified as 9 [ $\lambda_{\text{max}}$  (C<sub>6</sub>H<sub>14</sub>) 295 nm ( $\epsilon$  10,400)] and 10 [ $\lambda_{\text{max}}$  (C<sub>6</sub>H<sub>14</sub>) 257 ( $\epsilon$  5800)], were obtained in each case. These are obviously secondary products and are believed to originate from the trans-fused 8,9-dihydroindene shown in 11.



While the observed interconversion between 5 and 6 might, at first glance, be considered a serious mechanistic complication, closer scrutiny in terms of (i) the significantly faster (ca. 4x) thermolysis rate of the anti isomer, 5, (ii) the generation of the same mixture of isomeric 8,9-dihydroindenes from thermolysis of either 5 or 6 and (iii) well documented precedent<sup>3</sup>, establishes beyond reasonable doubt that it is the anti isomer, 5, in each case which is responsible for rearrangement of the system into an 8,9-dihydroindene skeleton. In full support of this interpretation we have succeeded in obtaining a reliable estimate of the observed  $t_{\text{max}}$  ( $90 \pm 5$  min.) relating to the transient buildup of 5 from 6, by

employing the known kinetic relationship:  $t_{\max} = \frac{1}{k_2 - k_1} \ln \frac{k_2}{k_1}$ , derived for a system of two consecutive first-order reactions. Solution of this equation with  $k_2 = k_a$  and  $k_1 = k_s$  yields  $t_{\max}$  (5) = 89 min.

Clearly, the present findings effectively substantiate the analysis of the situation hypothesized in the introductory section of this report and allow one to estimate the stabilizing influence of the cyano group on the cross-link of "folded" 1 at ca. 3.5 kcal/mole. Operationally this "cyano" effect is of course best rationalized in terms of the MO description recently advanced<sup>10</sup> to account for the existence of dicyanonorcaradiene.<sup>11</sup> Moreover, the kinetic manifestation of this effect in the case of 5 is clearly indicative of rate limiting involvement by the cross-link in the thermal rearrangement of "folded" cis-bicyclo [6.1.0] nona-2,4,6-trienes.

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- (6) The A<sub>2</sub>B pattern of this spectrum was fully reproduced by computer simulation techniques.
- (7) Thermolyses were conducted with neat samples in vacuum-sealed "Pyrex" tubes. The resulting thermolysates were analyzed and separated into their individual components by gas chromatography.
- (8) The rate of disappearance of reactant was monitored by nmr spectroscopy.
- (9) This substance was found to be stable to the reaction conditions.
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