at the sulfoxide oxygen.[15] The results, summarized in Table I, show that essentially all of the ^{18}O label (>90%)

Table I. ^{18}O-Labeling Results

Compound	^{18}O (atom % excess)[a] Sample 1	Sample 2
*O O ‖ ‖ $PhSCH_2OCPh$	6.4[b]	6.5[b]
$PhCO_2H$	5.7[c]	6.1[c]
O ‖ PhSOCPh	6.5[d]	6.4[d]

[a] Determined by direct mass spectrometry of the compounds; error = ±0.1%. [b] From *m/e* peaks 125/127 of **1**. [c] From molecular ion. [d] From *m/e* peaks 230/232 of **1**.

is found in the benzoic acid and indicate that the fragmentation reaction involves the cyclic zwitterionic intermediate of Scheme II. The slightly less than quantitative recovery of the ^{18}O label in benzoic acid may be the result of a small amount of exchange during work-up. The conclusion that all of the reaction follows Scheme II is supported by the observation that **1** fragments (probably thermally) in the mass spectrometer with loss of unlabeled formaldehyde to give *m/e* peaks 230/232 which are consistent with structure **3** containing all of the label.[16]

Acknowledgments. We wish to acknowledge the assistance of Dr. R. A. Upham of the University of Minnesota for performing the mass spectral analyses on our labeled compounds. We are indebted to the National Cancer Institute for support of this study (CA-13201-01).

(15) The method of sulfide oxidation with the pyridine–bromine complex and ^{18}O-enriched water was employed: S. Oae, Y. Ohnishi, S. Kozuka, and W. Tagaki, *Bull. Chem. Soc. Jap.*, **39**, 364 (1966).

(16) Mass spectral oxygen-18 analysis was not obtained for the paraformaldehyde because of its complex fragmentation pattern.

(17) National Science Foundation Undergraduate Research Participant, 1970.

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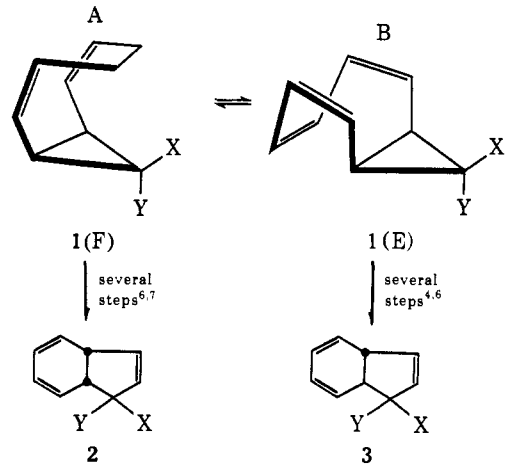
Thermal Bond Relocation of the *syn*- and *anti*-9-*tert*-Butylbicyclo[6.1.0]nona-2,4,6-trienes. Evidence for Strict Conformational Control

Sir:

A few years ago we stressed[1] the possible complexity of the seemingly straightforward, well documented,[2] conversion of *cis*-bicyclo[6.1.0]nona-2,4,6-triene (**1**; X = Y = H) into *cis*-bicyclo[4.3.0]nona-2,4,7-triene (**2**; X = Y = H) insofar as orbital symmetry[3] demands that the resulting [4.3.0] bicycle be fused trans rather than cis.[1] The first mechanistic breakthrough with regard to this bond relocation dates to the subsequent discovery, by Staley and Henry,[4] that 9,9-dialkylbicyclo[6.1.0]nona-2,4,6-trienes do indeed thermolyze to the expected trans-fused bicyclo[4.3.0]nona-2,4,7-trienes and the consequent realization by these workers that reactant conformation influences the stereochemical outcome of the general [6.1.0] to [4.3.0] conversion.[5] This notion was effectively confirmed and further amplified by our own efforts in the area[6,7] which established that (i) of the two 9-methylbicyclo[6.1.0]nona-2,4,6-triene variants only the syn isomer produces a significant amount (32%) of trans-fused 8,9-dihydroindene skeleton on thermolysis,[6] (ii) the thermal bond relocation of the parent [6.1.0] triene is somehow intermediated by *cis,cis,trans,cis*-cyclononatetraene,[7] and (iii) path A of Scheme I (abbreviated) is favored over

Scheme I



path B by a $\Delta\Delta G^{\ddagger}$ term of *ca.* 4 kcal/mol.[6,7]

Presently, we disclose pertinent information with the sterically demanding *syn*- and *anti*-9-*tert*-butylbicyclo[6.1.0]nona-2,4,6-trienes which constitutes the first unambiguous realization of the conformationally controlled mechanistic dichotomy postulated in Scheme I. Moreover, the work detailed here serves to effectively counter recent criticism[8] of our mechanistic interpretation of the thermolytic behavior of *syn*-9-methylbicyclo[6.1.0]nona-2,4,6-triene (**1**; X = CH_3, Y = H).

The two novel stereoisomeric *tert*-butyl derivatives[9] were prepared as shown in Scheme II: **4** [white crys-

(1) A. G. Anastassiou, *J. Amer. Chem. Soc.*, **90**, 1527 (1968); see also W. Grimme, Habilitationsschrift, Koln, 1968.

(2) E. Vogel, *Angew. Chem.*, **73**, 548 (1961); **74**, 829 (1962).

(3) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970.

(4) S. W. Staley and T. J. Henry, *J. Amer. Chem. Soc.*, **91**, 1239, 7787 (1969).

(5) For a critical evaluation of the problem, see S. W. Staley, *Intra-Sci. Chem. Rep.*, **5**, 149 (1971).

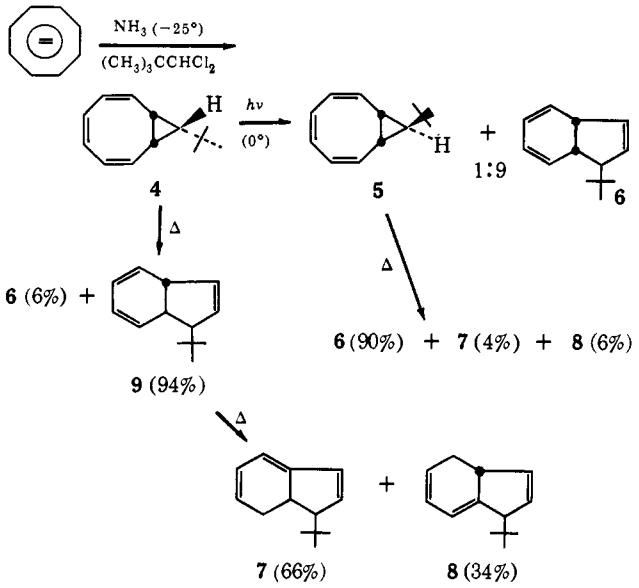
(6) A. G. Anastassiou and R. C. Griffith, *J. Chem. Soc. D*, 1301 (1971), 399 (1972).

(7) A. G. Anastassiou and R. C. Griffith, *J. Amer. Chem. Soc.*, **93**, 3083 (1971). In answer to a referee's comment, we note that as of this writing the above report contains the only *bona fide* example of cycloadditive trapping of *cis,cis,trans,cis*-CNT. We might recall in this context that the early mechanistic confusion associated with the formation of a cycloadduct incorporating a monocyclic C_9 moiety in the reaction of TCNE with *cis*-bicyclo[6.1.0]nona-2,4,6-triene (W. Okamura and T. W. Osborn, *J. Amer. Chem. Soc.*, **92**, 1061 (1970); C. S. Baxter and P. J. Garratt, *ibid.*, **92**, 1062 (1970)) has been effectively clarified with the recent demonstration (J. Clardy, L. K. Read, M. J. Broadhurst, and L. A. Paquette, *ibid.*, **94**, 2094 (1972)) that the stereochemical characteristics of the adduct are incompatible with its origination from *cis,cis,trans,cis*-CNT. In fact, Paquette and coworkers reasonably ascribe the formation of the said adduct to electrophilic addition of TCNE onto the *intact* [6.1.0]triene skeleton.

(8) M. B. Sohn, M. Jones, Jr., and B. Fairless, *J. Amer. Chem. Soc.*, **94**, 4774 (1972).

(9) Stereochemical assignments were made on the basis of the well documented tendency of the C-9 proton in an anti [6.1.0] stereoisomer to (i) resonate at higher field and (ii) exhibit a smaller coupling constant than its counterpart in the corresponding syn stereoisomer.

Scheme II



tals (mp 72–73°); ν(KBr): 2940, 1350, 1190, 989, 849, 808, 778, 758, 689 cm^{-1}; λ_{max} (C_6H_{14}): 252 nm (ϵ 3700); *m/e* 174 (P^+; 21%); nmr (60 MHz; $CDCl_3$): τ 3.8–4.2 (6 H, m), 8.44 (2 H, A_2 component of A_2B pattern), 8.88 (1 H, B component of A_2B pattern, J_{AB} = 10.0 Hz[10]), 9.0 (9 H, s)], **5** [colorless liquid; ν (neat): 2940, 1458, 1352, 779, 687 cm^{-1}; λ_{max} (C_6H_{14}): 248 nm (ϵ 3500); *m/e* 174 (P^+; 27%); nmr (60 MHz, benzene-d_6): τ 3.9–4.2 (6 H, m), 8.68 (2 H, d, J = 6 Hz), 9.21 (9 H, s), 9.69 (1 H, t, J = 6 Hz)], **6** [colorless liquid; ν (neat): 2950, 1465, 1350, 823, 782, 767, 713, 700, 675 cm^{-1}; λ_{max} (C_6H_{14}): 255 nm (sh) (ϵ 2800), 263.5 (ϵ 3600), 273 (ϵ 3400), 284 (sh) (ϵ 1800); *m/e* 174 (P^+; 28%); nmr (60 MHz, $CDCl_3$): τ 4.0–4.6 (6 H, m), 6.39 (1 H, d, J = 12 Hz), 7.06 (1 H, d, J = 12 Hz), 7.50 (1 H, s), 9.08 (9 H, s)].

The activation constants associated with the thermal rearrangement of **4** at 151° are $\Delta G^{\ddagger}$ = 31.8 kcal/mol and $k = 3.72 \pm 0.18 \times 10^{-4}$ sec^{-1}.[11] On exposure to 179° for 20 min **4** is quantitatively (>95%) converted to an isomeric mixture consisting of[12] 62% **7** [colorless liquid; λ_{max} (C_6H_{14}): 299 nm (ϵ 9900); *m/e* 174 (P^+; 21%); nmr (60 MHz, $CDCl_3$): τ 3.6–4.4 (5 H, m), 7.3–8.4 (4 H, m), 9.07 (9 H, s)],[13] 32% **8** [colorless liquid; λ_{max} (C_6H_{14}): 268.5 nm (ϵ 5400); *m/e* 174 (P^+; 13%); nmr (60 MHz, $CDCl_3$): τ 3.8–4.5 (5 H, m), 6.71 (1 H, dd, J = 18, 8 Hz), 7.02 (1 H, s), 7.7–8.4 (2 H, m), 9.1 (9 H, s)],[13] and 6% **6** (spectrally identical (ir, uv, nmr) with an authentic sample obtained from photolysis of **4**)[13] all of which were found to be stable under the reaction conditions. Significantly, brief (45 sec) thermolysis of **4** (*ca.* 5% consumption) leads to the trans-fused 8,9-dihydroindene (**9**) [colorless liquid; λ_{max} (C_6H_{14}): 261 nm (ϵ 3400); *m/e* 174 (P^+; 19%); nmr (100 MHz, $CDCl_3$): τ 3.5–3.7 (2 H, m), 4.0–4.3 (4 H, m), 7.0 (1 H, d, J = 20 Hz), 7.7–8.1 (2 H, m), 9.05 (9 H, s)].[13] Moreover, exposure of **9** to 179° for 10 min results in its essentially quantitative (>95%) conversion to **7** and **8** in a ratio of 2:1, respectively, *i.e.*, in the same proportion these two products materialize from prolonged thermolysis of **4**. Compound **4** is thus seen to isomerize almost exclusively (94%) to a trans-fused 8,9-dihydroindene frame.

The thermal rearrangement of **5** at 76.6° is controlled by the activation constants $\Delta G^{\ddagger}$ = 28.0 kcal/mol and $k = 2.36 \pm 0.10 \times 10^{-5}$ sec^{-1}. On being heated at 179° for 10 min, this isomer quantitatively bond relocates to a mixture consisting of[12] 90% **6**[14] (ir, uv, nmr), 4% **7**[15] (uv), and 6% **8**[15] (uv). The anti isomer (**5**) is thus seen to isomerize chiefly (90%) to a *cis*-8,9-dihydroindene frame, *i.e.*, **6**.

The present findings thus serve to demonstrate, unambiguously, for the first time that *given a sterically demanding nonpolar C(9) substituent, a pair of stereoisomeric 9-substituted cis-bicyclo[6.1.0]nona-2,4,6-trienes will bond relocate at widely different rates and along stereochemically distinct paths.* Moreover, our data effectively confirm our earlier estimate[6,7] that $\Delta G^{\ddagger}$ (B) − $\Delta G^{\ddagger}$ (A) be *ca.* 4 kcal/mol. Interestingly, orbital symmetry is seen to be fully preserved only along the high energy path![16]

Finally, it might be stressed that the stereospecificity observed in the present study demands that **4** and **5** preserve their stereochemical identity at the reaction temperature (179°) and that by analogy one is compelled to conclude that a syn to anti interconversion is equally inoperative in the case of the 9-methyl analogs.[6] It follows that the thermal conversion of *syn*-9-methylbicyclo[6.1.0]nona-2,4,6-triene (**1**; X = CH_3, Y = H) largely to a cis-fused 1-methyl-8,9-dihydroindene at a temperature as low as 110°[5] is most likely *not* due to a prerearrangement syn to anti isomerization as was recently suggested by others.[8] We must therefore adhere to our original suggestion[6] that the observed partial thermal conversion of **1** (X = CH_3, Y = H) largely to a cis-fused dihydroindene skeleton, *e.g.*, **2**, appears to be due to the relatively small steric "size"

(10) The A_2B pattern of this spectrum was fully reproduced by computer simulation techniques.

(11) The rate of disappearance of reactant was monitored by nmr spectroscopy.

(12) Thermolysis was carried out with a neat sample in a vacuum sealed Pyrex tube. The resulting thermolyzate was analyzed and separated into its individual components by gas chromatography.

(13) The spectral characteristics of this substance are entirely analogous to those reported for the monomethyl[6] and dimethyl[4] counterparts. Further, on exposure to air at ambient temperature this compound is converted to 1-*tert*-butylindene: colorless liquid; ν (neat): 2950, 1450, 1350, 1220, 797, 760, 736, 720 cm^{-1}; λ_{max} (C_6H_{14}): 255 nm (ϵ 7700), 283 (650) 290 (400); *m/e* 172 (P^+; 18%), nmr (60 MHz, $CDCl_3$): τ 2.3–3.0 (4 H, m), 3.18 (1 H, dd, J = 6, 2 Hz), 3.46 (1 H, dd, J = 6, 2 Hz), 6.73 (1 H, broad s), 8.97 (9 H, s).

(14) Under proper gc conditions the 1-*tert*-butyl-*cis*-8,9-dihydroindene may be shown to consist of both stereoisomeric forms with the specific stereoisomer produced from photolysis of **4** invariably predominating, 9:1. The minor stereoisomer was characterized by its uv spectrum which exhibits the four closely located characteristic maxima of a *cis*-8,9-dihydroindene.

(15) It is uncertain whether the **7**, **8** pair obtained here is identical or stereoisomeric with that produced on prolonged thermolysis of **4**. In fact, the different proportions in which **7** and **8** form in the two reactions (*ca.* 2:1 from **4** and 1:1.5 from **5**) may be indicative of the nonidentity of the two pairs, which would in turn imply that their *trans*-8,9-dihydroindene precursors are also stereoisomeric. This is not inconceivable inasmuch as the two possible monocyclic precursors of 1-*tert*-butyl-*trans*-8,9-dihydroindene (9-*tert*-Bu-*cis,cis,trans,cis*-CNT in path A and 9-*tert*-Bu-*cis,cis,cis,trans*-CNT in path B) are geometrically isomeric rather than identical. The scarcity of **5** coupled with the trace amounts in which **7** and **8** form from the thermolysis of this substance have precluded an assessment of stereochemical detail at this stage.

(16) It is pertinent to stress in this connection that while the disallowed step in A is undoubtedly associated with the generation *cis,cis,cis,cis*-CNT, a well documented thermal progenitor of the *cis*-8,9-dihydroindene frame (**2**), the exact source of this monocycle has yet to be rigorously demonstrated. In principle, it may directly materialize from disrotatory cross-link scission of a folded [6.1.0][4,17] or [5.2.0][6,7] trienic skeleton.

(17) A. G. Anastassiou and E. Yakali, *J. Amer. Chem. Soc.*, **93**, 3803 (1971).

of the methyl group,[18] which allows it to be forced into the cavity of the folded form, **1** (X = CH_3, Y = H) (F) with consequent partitioning of the bond relocation along both possible paths, A and **B**, with a slight preference (70:30) for A.[19]

Acknowledgment. We wish to thank the National Science Foundation (GP-26347) and the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

(18) For a rational explanation as to why a syn methyl substituent o a monomethyl bridge ought to be sterically "smaller" than one associ ated with a dimethyl group see ref 4.

(19) Perhaps it is worth stressing here that the present invalidation of the criticism leveled at this interpretation serves as a clear warning against the use of readily available, but improperly substituted compounds as models for securing mechanistic information about skeletal transformations of hydrocarbons. This cautionary note is perhaps best exemplified by the exclusive thermal bond relocation of 9-methyl-9-cyanobicyclo[6.1.0]nona-2,4,6-triene[20] and its dicyano analog[21] into a [4.2.1] rather than [4.3.0] skeleton.

(20) F. G. Klärner, *Tetrahedron Lett.*, 3611 (1971).

(21) A. G. Anastassiou, R. P. Cellura, and E. Ciganek, *Tetrahedron Lett.*, 5267 (1970).

(22) National Science Foundation Graduate Trainee, 1969–present.

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Thermal Rearrangement of *cis*-Bicyclo[6.1.0]nona-2,6-dienes

Sir:

Recently the protection of suitably located double bonds in catalytic hydrogenations by means of the trifluoroacetylacetonatorhodium group has been demonstrated.[1] This synthetic method, when applied to *cis*-bicyclo[6.1.0]nona-2,4,6-trienes, makes the corresponding *cis*-bicyclo[6.1.0]nona-2,6-dienes readily accessible.

According to Scheme I the trienes **1a–d**[2] were transformed into the trifluoroacetylacetonatorhodium(I) complexes **2a–d** by treatment with dicarbonyltrifluoroacetylacetonatorhodium in hexane solution. The free double bond in these complexes was hydrogenated in hexane solution with 5% Pd/C, and the olefinic ligand was set free from the resulting complexes **3a–d** by shaking a pentane solution with 10% aqueous KCN. Data for the individual reaction steps are listed in Table I.

The *cis*-bicyclo[6.1.0]nona-2,6-dienes **4a–d** thus obtained undergo thermal rearrangement to the respective *cis*-bicyclo[5.2.0]nona-2,5-dienes **5a–d** under distinctly different conditions.

Whereas **4a**[3] and its *anti*-9-methyl derivative **4b** undergo the Cope rearrangement to **5a**[4] and **5b**, respectively, already at room temperature, the *syn*-9-methyl compound **4c** requires 150° for its transformation into **5c** and the *gem*-dimethyl compound **4d** rearranges only above 180°. In the latter case a by-product, believed to be 3-(2-propenyl)cycloocta-1,4-diene, appears for whose formation a competing homopentadienyl hydrogen shift[4,5] in **4d** can be envisioned. The unidirectional Cope rearrangement of the parent compound **4a** turns reversible in the methyl derivatives **4b–d**. This stabilization of a cyclopropane ring by methyl substitution is well documented both by theory[6] and experiment.[7] Judging from the equilibrium constants for the isomerization of 1-methylbarbaralone[7] and of dienes **4b–d** (see Table II), a methyl group favors a cyclopropane ring over a bisallylic position by 0.7–2.5 kcal/mol in free energy. Accordingly, the parent compound **4a** already must be close to equilibrium with **5a**.

The stereospecificity of the rearrangement follows from the fact that epimeric products arise from **4b** and

Scheme I

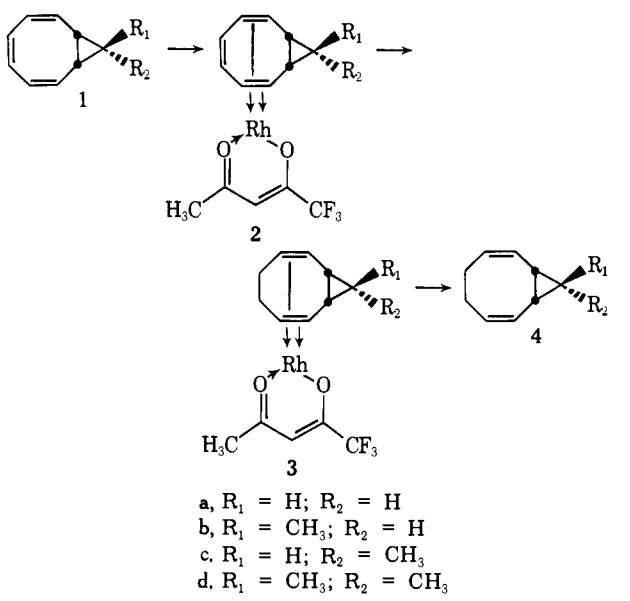
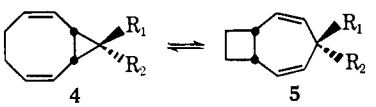


Table I. Selective Reduction of *cis*-Bicyclo[6.1.0]nonatrienes

Starting triene	Yield (%) (mp, °C) of intermediates 2	3		Yield (%) and ^{1}H nmr data[a] of product 4 R_1	R_2
1a	94.5 (64)	88 (67)	85[b]	9.18, t of d (9; 3.5)	9.98, t of d (6.5; 3.5)
1b	88.5 (89)	90.5 (105)	76[b]	8.85, d (6)	9.63, q (6)
1c	93 (87)	88 (98)	68	8.8–9.2, m	9.10, d (2.5)
1d	97 (109)	86.5 (110)	82	8.86, s	9.10, s

[a] Reported are the shifts (τ) and coupling constants (Hz) of the groups R_1 and R_2, determined in CCl_4 solution with benzene as internal standard at 100 MHz; other signals are in accord with the structure. [b] Liberation and work-up at 0°.



(1) W. Grimme, *J. Amer. Chem. Soc.*, **94**, 2525 (1972).

(2) (a) E. Vogel and H. Kiefer, *Angew. Chem.*, **73**, 548 (1961); (b) T. J. Katz and P. J. Garratt, *J. Amer. Chem. Soc.*, **86**, 4876 (1964); (c) P. Radlick and W. Fenical, *ibid.*, **91**, 1560 (1969); (d) J. Esser, Diplomarbeit, University of Cologne, 1968; (e) S. W. Staley and T. J. Henry, *J. Amer. Chem. Soc.*, **91**, 1239 (1969).

(3) The synthesis of **4a** by a more laborious route and its rearrangement have been reported: M. S. Baird and C. B. Reese, *Chem. Commun.*, 1519 (1970).

(4) W. R. Roth, *Justus Liebigs Ann. Chem.*, **671**, 10 (1964).

(5) (a) W. Grimme, *Chem. Ber.*, **98**, 756 (1965); (b) D. S. Glass, R. S. Boikess, and S. Winstein, *Tetrahedron Lett.*, 999 (1966).

(6) N. Trinajstić and M. Randić, *J. Chem. Soc.*, 5621 (1965).

(7) J. C. Barborak, S. Chari, and P. von R. Schleyer, *J. Amer. Chem. Soc.*, **93**, 5275 (1971).