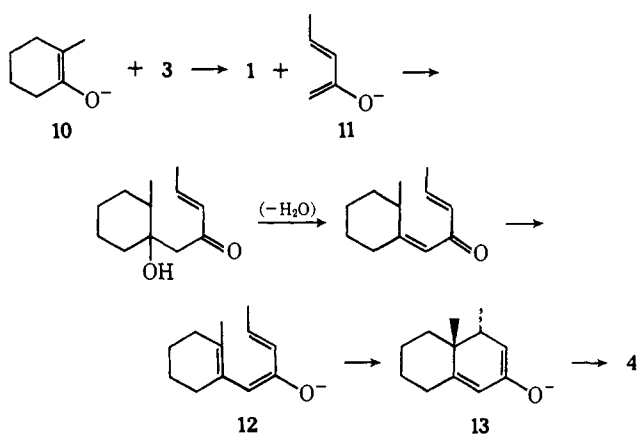


## Scheme I



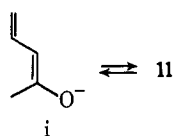
disrotatory cyclization<sup>16</sup> of **12** to **13**, essentially the reverse of the normally accepted steps in the Robinson annulation reaction.<sup>1,17</sup> Since enolates derived from homologs of 2-carbomethoxycyclohexanone (**2**) are considerably more stable than the enolate of **3**, Scheme I would not be expected to be operative in those cases. In the above case, however, the cross-conjugated enolate **11**<sup>18</sup> is probably more stable than the enolate derived from 2-methylcyclohexanone (**10**). Moreover, initial Michael addition of **10** to **3** would be expected to be retarded significantly due to increased steric congestion (relative to methyl vinyl ketone) at the  $\beta$ -carbon atom of **3**. Further experiments designed to verify the validity of the steps proposed in Scheme I are currently in progress in our laboratories.

**Acknowledgments.** We are indebted to Professor C. Djerassi of Stanford University and to Dr. W. S. Knowles of the Monsanto Chemical Company for generous gifts of *d-trans*-4-camphorsulfonyloxy-3-methoxy-9-methyl-2,6-hexal-1-one<sup>12,19</sup> used in the preparation of an authentic sample of decalone **8**.

(16) (a) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, Weinham/Bergstr., Germany, 1970, Chapter 5. (b) It is of interest that the conversion **10**  $\rightarrow$  **11** is analogous in many respects to the cyclization described by Woodward [R. B. Woodward, *Chem. Soc. Spec. Publ.*, No. 21, 217 (1967)] which ultimately led to the concepts of the conservation of orbital symmetry. (c) The *trans*-1,9-dimethyldecalin ring system has recently been prepared via cyclization of a related triene system [R. Ramage and A. Sattar, *Chem. Commun.*, 173 (1970)].

(17) That the steps in the Robinson annulation reaction might be an aldol condensation followed by an intramolecular Michael reaction, instead of the reverse, has been alluded to previously [R. B. Woodward and T. Singh, *J. Amer. Chem. Soc.*, 72, 494 (1950)].

(18) The formation of the alternative enolate **i** probably occurs even more readily than **11**. Since products derived from **i** are not observed, its formation does not affect the above argument as long as a rapid equilibrium between the two enolates is established.<sup>14</sup>



(19) A. J. Speziale, J. A. Stephens, and Q. E. Thompson, *J. Amer. Chem. Soc.*, 76, 5011 (1954).

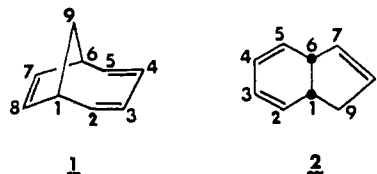
Charles J. V. Scanio,\* Richmond M. Starrett  
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Received January 14, 1971

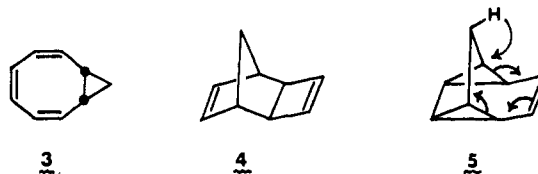
## Pyrolytic Transformation of Bicyclo[4.2.1]nona-2,4,7-triene to Bicyclo[4.3.0]nona-2,4,7-triene (*cis*-8,9-Dihydroindene). The "Hydrogen-Rebound" Pathway of Thermal Rearrangement<sup>1</sup>

Sir:

The pyrolysis of bicyclo[4.2.1]nona-2,4,7-triene (**1**) at temperatures above 290° in either the gas phase or dodecane solution causes rearrangement to bicyclo[4.3.0]nona-2,4,7-triene (*cis*-8,9-dihydroindene, **2**).<sup>2</sup> Most of the plausible hypothetical mechanisms for this reaction fall into two categories: (i) an all-carbon sigmatropic process, such as [1,3]- or [1,5]-sigmatropic rearrangement to *cis*-bicyclo[6.1.0]nona-2,4,6-triene (**3**),



which is known<sup>3</sup> to rearrange readily to **2**, or isomerization of **1** to its tricyclic valency tautomer **4**<sup>4</sup> followed by sigmatropic rearrangement of the type recently reported in another system;<sup>5</sup> (ii) a process initiated by an intramolecular Diels-Alder reaction (**1**  $\rightarrow$  **5**)<sup>2b</sup> and completed by overall hydrogen shift (**5**  $\rightarrow$  **2**).



Experiments with the deuterium-labeled substance 1-7,8-*d*<sub>2</sub> permit in principle a distinction between these two mechanistic categories. Category i gives product **2** with at least one olefinically bound deuterium, whereas category ii gives **2** with deuterium bound exclusively to paraffinic carbon. Pyrolyses of two samples of 1-7,8-*d*<sub>2</sub> give product **2** with olefinic-paraffinic proton magnetic resonance intensity ratios of 2.07 and 2.21, as compared to theoretical values of 1.310 and 1.325 for mechanistic category i and 2.727 and 2.567 for

(1) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work. We are also grateful to the National Science Foundation for partial support through an institutional grant (No. GU-3282).

(2) (a) Side products include indan, indene,  $\beta$ -methylstyrene, and allylbenzene, all of which are formed in the pyrolysis of **2** itself. Prolonged pyrolysis leads to extensive polymerization. (b) For a rearrangement of 9-phenyl-9-acetoxycyclo[4.2.1]nona-2,4,7-triene to 2-phenylindene, see T. S. Cantrell and H. Shechter, *J. Amer. Chem. Soc.*, 89, 5868 (1967).

(3) (a) E. Vogel and H. Kiefer, *Angew. Chem.*, 73, 548 (1961); (b) references to several other examples of this rearrangement in substituted derivatives of **3** are given by: S. W. Staley and T. J. Henry, *J. Amer. Chem. Soc.*, 91, 1239 (1969), and P. Radlick and W. Fenical, *ibid.*, 91, 1560 (1969).

(4) For the reverse of this (**4**  $\rightarrow$  **1**), see (a) L. G. Cannell, *Tetrahedron Lett.*, 5967 (1966); (b) H. M. Frey, J. Metcalfe, and J. M. Brown, *J. Chem. Soc. B*, 1586 (1970).

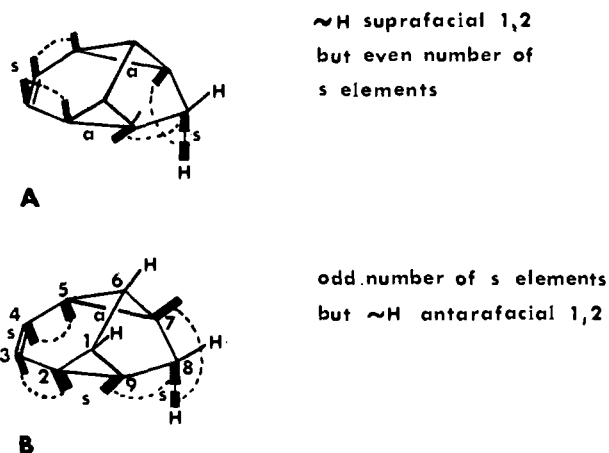
(5) E. Vedejs, *Tetrahedron Lett.*, 4963 (1970).

(6) (a) Prepared by treatment of *exo-trans-endo*-dinorbornadiene<sup>6b</sup> (kindly supplied by Dr. D. J. Trecker of Union Carbide Co., Inc.) with *n*-butyllithium in cyclohexylamine-*N,N*-*d*<sub>2</sub> and pyrolysis<sup>6a</sup> of the resulting olefinically deuterated<sup>7</sup> dimer. (b) Cf. D. R. Arnold, D. J. Trecker, and E. B. Whipple, *J. Amer. Chem. Soc.*, 87, 2596 (1965).

(7) H. E. Zimmerman, R. W. Binkley, R. S. Givens, G. L. Grunewald, and M. A. Sherwin, *ibid.* 91, 3316 (1969).

category ii. The observed value is too high to permit exclusive operation of category i and implicates the intramolecular Diels-Alder mechanism *via* tetracyclic olefin **5** as a major pathway.<sup>8</sup>

In the conversion of **5** to **2**, can the hydrogen transfer be concerted with the cleavage of both C-C bonds? Regardless of mechanistic details, simple geometric factors impose the condition that all the newly created double bonds of the product **2** must be *cis*. Only two types of concerted transition state can be constructed with orbitals that meet the *cis* double bond requirement. One, A, involves a suprafacial vicinal hydrogen shift but an *even* number of symmetric (*s*) reaction elements and therefore is "forbidden" by orbital symmetry.<sup>9</sup> The other, B, employs an odd number of *s* elements but now must use an antarafacial vicinal hydrogen shift and therefore is sterically difficult. Similar conclusions apply to processes in which the other methylene hydrogen migrates. However, it might be possible to effect the **5** → **2** rearrangement by *two successive "allowed" 1,5-homodieryl hydrogen shifts, viz., 5 → **6** → **2** (Scheme I). This hypothetical process would result again in overall shift of the circled hydrogen to a vicinal position, but only by an indirect pathway which involves initial transannular shift to give **6** followed by "rebound" of the same hydrogen to its ultimate lodgment at C-3 of **2**. We find that pyrolysis at 293° of hypothetical intermediate **6**, independently synthesized<sup>10</sup> in six steps from 1,4-dihy-*



drobenzoic acid, gives **2** quantitatively at a rate at least 65 times that of the **1** → **2** reaction. Diene **6** is therefore a permissible intermediate in the **1** → **2** rearrangement.

The pyrolysis of tricyclic diene **6** does not produce appreciable quantities of bicyclic triene **1**. Since it is likely that any of the tetracyclic olefin **5** formed from **6** would revert immediately to **1**,<sup>11</sup> the absence

(8) Starting material 1-7,8-*d*<sub>2</sub> is recovered with no detectable deuterium position rearrangement from partial pyrolysis. This excludes a competing [1,3]-degenerate rearrangement of 1-7,8-*d*<sub>2</sub> to 1-2,3-*d*<sub>2</sub>, which if it occurred, would lower the intensity ratio in the ultimate product **2**. Similarly, independently synthesized labeled product 2-2,3,4,5-*d*<sub>4</sub> is recovered with an intact labeling pattern after pyrolysis. The ratio in **2** obtained from 1-7,8-*d*<sub>2</sub> must therefore result either from a mixture of i and ii or from partial position mixing in an intermediate.

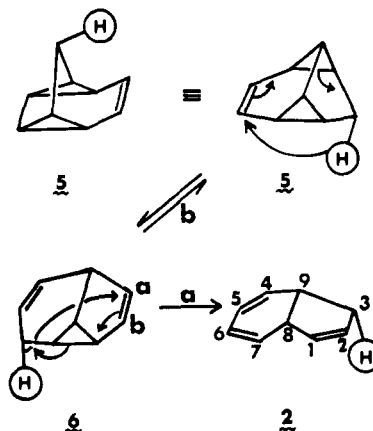
(9) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970.

(10) R. R. Boettcher, Ph.D. Thesis, University of Wisconsin, 1970.

(11) Olefin **5** is probably an intermediate in the formation of **1** by pyrolysis of the sodium salt of cycloheptatrienylacetaldehyde *p*-toluenesulfonylhydrazone.<sup>12</sup> Strong support for a facile **5** → **1** reaction also

of **1** suggests that if **6** is an intermediate in the **1** → **2** rearrangement (Scheme I), it must execute the second

Scheme I



hydrogen transfer to point a (reaction **6** → **2**) much faster than the reverse of the first (transfer to b, reaction **6** → **5**). The first hydrogen transfer (reaction **5** → **6**) then must be the overall rate-determining step in the **1** → **2** rearrangement by this mechanism.

Molecular models indicate that the circled hydrogen in **6** must leap about 2.8 Å to point a, but only about 2.3 Å to point b. Nevertheless, path a is preferred, presumably because of the exothermicity of the **6** → **2** reaction.

It seems likely that the "hydrogen-rebound" mechanism may provide an indirect but convenient device by which rearranging systems in the C<sub>n</sub>H<sub>n+1</sub> (*n* odd) series can avoid "forbidden" reactions. Such hydrogen shifts may thereby facilitate deep-seated carbon skeletal rearrangements.

comes from observations of the analogous transformations of tetracyclo[4.4.0.0<sup>2,10</sup>.0<sup>6,7</sup>]deca-3,8-dienes to bicyclo[4.2.2]deca-2,4,7,9-tetraenes.<sup>13-15</sup>

(12) H. Tsuruta, K. Kurabayashi, and T. Mukai, *J. Amer. Chem. Soc.*, **90**, 7167 (1968).

(13) M. Jones, Jr., and B. Fairless, *Tetrahedron Lett.*, 4881 (1968).

(14) S. Masamune, R. T. Seidner, H. Zenda, M. Wiesel, N. Nakatsuka, and G. Bigam, *J. Amer. Chem. Soc.*, **90**, 5287 (1968).

(15) (a) W. Grimme, H. J. Riebel, and E. Vogel, *Angew. Chem.*, **80**, 803, 823 (1968); (b) E. Babad, D. Ginsburg, and M. B. Rubin, *Tetrahedron Lett.*, 2361 (1968); (c) J. Altman, E. Babad, M. B. Rubin, and D. Ginsburg, *ibid.*, 1125 (1969); (d) J. S. McConaghy, Jr., and J. J. Bloomfield, *ibid.*, 1121 (1969).

(16) Supported by Postdoctoral Fellowship No. FO2 AM 36193-02 from the National Institute of Arthritis and Metabolic Diseases.

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## Isoracemization of *N*-Carbobenzoxyamino Acid Ester Derivatives

Sir:

We wish to report that the racemization by  $\alpha$ -hydrogen abstraction of two *N*-carbobenzoxyamino acid active esters in a nonpolar solvent proceeds *via* isoracemization in the presence of triethylamine. We recently reported that racemization of *N*-carbobenzoxy-S-benzyl-L-cysteine active esters does not proceed