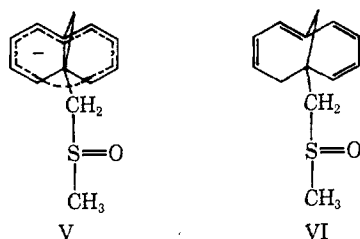


monohomotropylium ion.<sup>1</sup> Furthermore, the average chemical shift of the bridge protons,  $\tau$  8.10, is only 0.24 ppm downfield from the average shift of the bridge protons of III,  $\tau$  8.34,<sup>10</sup> hardly an impressive deshielding when compared to the shielding of the bridge protons (2.88 ppm) of the homoaromatic V, relative to VI.<sup>12</sup>



The second question of electronic structure is what is the extent of  $C_1$ - $C_6$  overlap (*i.e.*, what is the  $C_1$ - $C_6$  distance or the  $C_1$ - $C_{11}$ - $C_6$  bond angle)?<sup>13</sup> The usual nmr criterion for such overlap is the size of  $J_{11a,11b}$ .<sup>7b</sup> Thus, since  $|J_{11a,11b}|$  for II (9.3 Hz) is larger than for I ( $|J_{11a,11b}| = 7.0$  Hz),<sup>14</sup> one is tempted to conclude that there is less 1,6 overlap in II than I. Recently, however, some doubt was cast on the validity of the above concept by the report that the chromium tricarbonyl complex of I [ $I-Cr(CO)_3$ ], whose  $C_1$ - $C_6$  distance is known<sup>15</sup> to be 0.12 Å shorter than that of I, has a larger  $|J_{11a,11b}|$  (8.9 Hz)<sup>16</sup> than I. On the other hand,  $J_{11C_{11},H_{11}}$  ( $147 \pm 1$  Hz)<sup>16</sup> for  $I-Cr(CO)_3$  is larger than that for I ( $J_{11C_{11},H_{11}} = 142 \pm 2$  Hz),<sup>14</sup> as is expected for a decreased  $C_1$ - $C_6$  distance.  $J_{11C_{11},H_{11}}$  ( $148 \pm 1$  Hz)<sup>17</sup> for II is also larger than that for I. In fact, the coupling constant data for  $C_{11}$  in II bear a strikingly close resemblance to those for  $C_{11}$  in  $I-Cr(CO)_3$ . Thus, we tentatively conclude that the  $C_1$ - $C_6$  distance in II may be smaller than in I. However, it seems clear that the extent of  $C_1$ - $C_6$  overlap in II is much less than in IV (same number of  $\pi$  centers in the ring), which exists in the closed form ( $J_{11a,11b} = 4.5$  Hz).<sup>6</sup> This smaller overlap is readily understood, since increasing the  $\sigma$  character of the  $C_1$ - $C_6$  interaction serves to localize charge on  $C_3$ ,  $C_4$ , and  $C_5$ . This is particularly harmful since the charge is removed from  $C_1$ , which is a tertiary position (and thus best able to bear positive charge).

We find that dissolving I in  $FSO_3D-SO_2$  ClF gives rise to II- $d_1$ , where the deuteron replaces the proton whose resonance is at  $\tau$  5.54 ( $H_{2a}$ ). The stereoselectivity is greater than 96% (60-MHz nmr integration). Unfortunately, it is not possible to determine which side of I the incoming proton attacks, since two final conformations are possible for II.<sup>18</sup> In the first, the methylene group ( $C_2$ ) is tipped upward, toward  $C_{11}$ . If this is the conformation, then the incoming proton must attack from the bottom side of the molecule (*trans* to  $C_{11}$ ).

(12) W. A. Böll, *Tetrahedron Lett.*, 5531 (1968).

(13) It is noteworthy that as  $C_1$  and  $C_6$  come together, they do so in a manner that increases the  $\sigma$ -type overlap of their p orbitals, ultimately resulting in the formation of a cyclopropane banana bond.

(14) H. Günther, *Z. Naturforsch.*, B, 20, 948 (1965).

(15) P. E. Baikie and O. S. Mills, *Chem. Commun.*, 683 (1966).

(16) H. Günther, R. Wenzl, and W. Grimme, *J. Amer. Chem. Soc.*, 91, 3808 (1969).

(17) Obtained, at 60 MHz, after summation of 100 scans by the Time Averaging Computer.

(18) This is based on the fact that  $H_{2b}$  and  $H_3$  must have a dihedral angle of ca.  $90^\circ$ <sup>19</sup> between them, since  $J_{2b,3}$  is ca. 0 Hz. The conformations were derived from examination of models.

(19) E. Garbisch, Jr., *J. Amer. Chem. Soc.*, 86, 5561 (1964).

This might be favorable due to the greater electron density beneath I.<sup>20</sup> The other conformation has  $C_2$  bent downward, away from  $C_{11}$ . If this conformation is the correct one, then the proton attacks from the top side of I. This latter conformation seems to allow better overlap among the p orbitals of  $C_5$ ,  $C_6$ , and  $C_7$ . It is important to note that the data only allow one of the two conformations to be present in large amounts; however, examination of models indicates no great barrier should exist for their interconversion (*i.e.*, one conformer must be more stable than the other).

It would be interesting to observe the higher annulenes in strong acid. Work in that direction is currently in progress in these laboratories.

**Acknowledgment.** We are grateful to Dr. David Harris for assistance in taking the 100-MHz nmr spectra.

(20) In the analogous protonation of 1,6-methanocyclononatetraenyl anion [P. Radlick and W. Rosen, *ibid.*, 89, 5308 (1967)], the incoming proton was found to attack from the bottom.

(21) National Science Foundation Predoctoral Fellow, 1966-1969.

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#### Evidence for a *cis,cis,cis,trans*-Cyclononatetraene in the Thermal Reorganization of 9-Ethyl-9-methyl-*cis*-bicyclo[6.1.0]nona-2,4,6-triene

Sir:

The facile thermal reorganization of *cis*-bicyclo[6.1.0]nona-2,4,6-trienes to *cis*-8,9-dihydroindenes has stimulated a great deal of interest,<sup>1,2</sup> primarily because the most reasonable mechanism is not in accord with the orbital symmetry rules for concerted reactions.<sup>3</sup> We have recently reported the first example of the reorganization of a *cis*-bicyclo[6.1.0]nona-2,4,6-triene in which a *trans*-8,9-dihydroindene is obtained as the major product ( $1a \rightarrow 2a$ ).<sup>1</sup> The mechanism of this reaction is of interest because there are several conceivable "symmetry allowed" pathways and also because its elucidation should provide additional insight into the mechanism of formation of *cis*-8,9-dihydroindenes.<sup>2</sup>

(*E*)- and (*Z*)-9-ethyl-9-methyl-*cis*-bicyclo[6.1.0]nona-2,4,6-triene<sup>4</sup> (**1b** and **1c**, respectively) were obtained in 67% yield as a 1.5:1 mixture by the general method described previously.<sup>1</sup> The separation of these isomers was a difficult task but was successfully accomplished by employing two different gas chromatography (glpc) columns, *viz.* 20% DEGA on  $\text{E0-100}$  Diatoport S and 20% Carbowax 20M on 100-120 silanized Chromosorb P. Both products exhibited negative distribution isotherms<sup>5</sup> (steep front peak edge) on the former column at  $130^\circ$ , which permitted the purification of **1b** (eluted first), and positive isotherms on the latter column at

(1) S. W. Staley and T. J. Henry, *J. Amer. Chem. Soc.*, 91, 1239 (1969), and references cited therein.

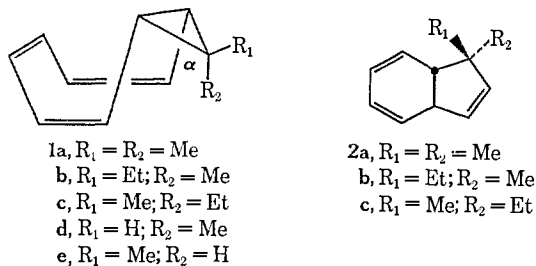
(2) P. Radlick and W. Fenical, *ibid.*, 91, 1560 (1969).

(3) R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, 1, 17 (1968).

(4) For a discussion of the nomenclature see J. E. Blackwood, C. L. Gladys, K. L. Loening, A. E. Petrarca, and J. E. Rush, *J. Amer. Chem. Soc.*, 90, 509 (1968).

(5) A. I. M. Keulemans, "Gas Chromatography," 2nd ed, Reinhold Publishing Corp., New York, N. Y., 1959, Chapter 4.

105°, thereby allowing the isolation of **1c**.<sup>6</sup> These isomers have been assigned the (*E*) (**1b**) and (*Z*) (**1c**) structures by comparison of the methyl proton chemical shifts ( $\tau$  9.08 and 8.85, respectively) with those of the corresponding signals for **1d** and **1e** (9.007 and 8.79, respectively).<sup>8,9</sup>



When **1b** or **1c** was heated (neat) for 5 min at 170°, analysis by glpc showed four new peaks in an approximate ratio of 10:1:1:0.2; the proportion of the three minor components was <3% of the major one after only 45 sec.<sup>10</sup> Of particular interest is the fact that the major component is, in each case, a 1.8:1 mixture of (*E*)- and (*Z*)-1-ethyl-1-methyl-*trans*-8,9-dihydroindene (**2b** and **2c**, respectively). The nmr spectrum (CCl<sub>4</sub>) of this mixture is, with the exception of the ethyl proton signals, nearly identical with that of **2a**: multiplet at  $\tau$  3.6–4.5 (6 H, vinyl), AB quartet at 7.31 (2 H, bridgehead,  $J_{AB} = 20$  Hz), multiplet (with 3 major peaks) centered at 8.6 (2 H, methylene), singlets at 8.90 and 9.07 (3 H, methyl, peak height ratio = 1:1.8), and distorted triplet at 9.90 (3 H, methyl,  $J = 7$  Hz). The uv spectrum ( $\lambda_{\text{max}}^{\text{hexane}} 260.5$  nm ( $\epsilon$  3340)) also agrees with those for **2a**<sup>1</sup> and for *trans*-8,9-dihydroindene.<sup>11</sup> Because of (a) the large value for  $J_{89}$  (relative to that for *cis*-8,9-dihydroindene and its *syn*- and *anti*-1-methyl<sup>2</sup> and 1,1-dimethyl<sup>10</sup> derivatives), (b) the difference in the uv spectra of *trans*-8,9-dihydroindene (which has a single broad maximum)<sup>11</sup> and its *cis* isomer (which has two major peaks,<sup>12</sup> and (c) in view of the fact that **2a** has already been related to *trans*-1,1-dimethylhydrindan,<sup>1</sup> it is clear that **2b** and **2c** possess a *trans*-ring fusion. The major isomer (**2b**) has been tentatively assigned the (*E*) structure since, for steric reasons,<sup>13</sup> a methyl group is more likely than an ethyl group to adopt the *endo*

(6) We suggest that the application of this strategy in preparative chromatography may, in certain instances, greatly facilitate difficult separations.

(7) T. J. Katz and P. J. Garratt, *J. Amer. Chem. Soc.*, **86**, 4876 (1964). Cf. also the methyl chemical shifts in **1a**.<sup>1</sup>

(8) There is a transposition of numbers in the chemical shift reported for the methyl group in **1e**.<sup>9</sup> The C<sub>1</sub> and C<sub>6</sub> protons appear as a doublet centered at  $\tau$  8.89 ( $J = 7$  Hz) which overlaps the methyl doublet ( $J = 6$  Hz).

(9) All spectral data (ir, uv, nmr, and mass) are consistent with the assigned structures.

(10) Nmr analyses of the second and third components indicated that they are mixtures of the (*E*) and (*Z*) isomers of 1-ethyl-1-methyl-4,9-dihydroindene and 1-ethyl-1-methyl-7,8-dihydroindene. Formation of 1-ethyl-1-methylindene may occur if oxygen is not rigorously excluded. It is reasonable that the *cis*-8,9-dihydroindene isomers are not major products since we have found that the 1% unidentified product from **1a**<sup>1</sup> has the same retention time as *cis*-1,1-dimethyl-8,9-dihydroindene. The latter compound ( $\lambda_{\text{max}}^{\text{hexane}} 255$  nm (sh) ( $\epsilon$  2860), 263.5 (3640), 272.5 (3410), and 282 (sh) (1800); nmr:  $J_{89} = 13$  Hz) was obtained from the photolysis (Hanovia apparatus) of **1a** and is stable for at least 1 hr at 151°.

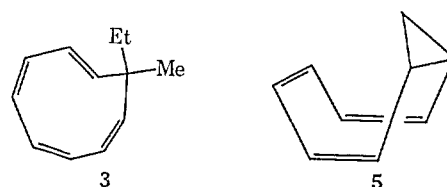
(11) J. Schwartz, *Chem. Commun.*, 833 (1969).

(12) T. J. Katz and P. J. Garratt, *J. Amer. Chem. Soc.*, **86**, 5194 (1964).

(13) J. A. Hirsch in "Topics in Stereochemistry," Vol. 1, N. L. Alinger and E. L. Eliel, Ed., John Wiley & Sons, Inc., New York, N. Y., 1967, pp 204–206.

position. In addition, the quasi-equatorial *exo* methyl should have a lower chemical shift than the quasi-axial *endo* methyl since models indicate that the former is closer to the nodal planes of the C<sub>2</sub>C<sub>3</sub> and C<sub>6</sub>C<sub>7</sub> double bonds.

We have established by glpc analysis that **1b** and **1c** are not interconverted under the reaction conditions. In addition, the product isomers (**2b** and **2c**) were partially separated by glpc and shown by nmr analysis not to be interconverted under the above conditions. These results demand a mechanism in which the stereochemical integrity of C<sub>9</sub> is lost during the course of the rearrangement. This requirement is best accommodated by the intermediacy of a *cis,cis,cis,trans*-cyclononatetraene (**3**) which can arise by a conrotatory opening and then close in a disrotatory sense in either of two directions to afford **2b** and **2c**. Each of these steps is "symmetry allowed."<sup>3,14</sup> A direct [1,3]-antarafacial sigmatropic migration of C<sub>1</sub> with retention of configuration is excluded by these results.<sup>15,17</sup>



Evidence has been presented that *cis*-8,9-dihydroindenes are formed (thermally) from *cis*-bicyclo[6.1.0]nona-2,4,6-trienes by disrotatory closure of all-*cis*-1,3,5,7-cyclononatetraenes (**4**).<sup>2,18</sup> However, direct disrotatory opening of the starting material to **4** is not a "symmetry allowed" pathway.<sup>19</sup> Several authors have discussed the possibility that intermediates analogous to **3** may form initially and then isomerize to **4**.<sup>2,20,21</sup> This mechanism may be excluded on the basis of the present results, which strongly suggest that **3** is converted to **2b** and **2c** and not to **4**.

(14) S. I. Miller, *Progr. Phys. Org. Chem.*, **6**, 210 (1968).

(15) The geometry of conformation **1** is nearly "ideal" for a hypothetical [1,3]-antarafacial sigmatropic migration of C<sub>1</sub> with retention of configuration; cf. the HCCH dihedral angles (estimated from models)  $\phi_{67}$  (0°) and  $\phi_{78}$  (105°) in **1** and  $\phi_{23}$  (90°) and  $\phi_{34}$  (0°) in **2**. This reaction can also be viewed as a four-electron "Möbius" activated complex (*i.e.*, it has one inversion of phase and is therefore allowed)<sup>16a</sup> or as a  $\sigma_s^2 + \pi_A^2$  cycloaddition process,<sup>16b</sup> also allowed. A referee has stated that this process would lead to a *cis*-8,9-dihydroindene. However, the  $\sigma_s^2 + \pi_A^2$  process which leads to a *cis*-ring fusion also gives a *trans* double bond in the five-membered ring of **2**; this can be rejected on steric grounds.

(16) (a) H. E. Zimmerman, *J. Amer. Chem. Soc.*, **88**, 1564, 1566 (1966); (b) R. B. Woodward and R. Hoffmann, *Angew. Chem.*, **81**, 797 (1969).

(17) A referee has suggested that a *cis,cis,trans,cis*-1,3,5,7-cyclononatetraene is a possible intermediate. Such an intermediate could conceivably arise by conrotatory opening of initially formed *cis*-bicyclo[5.2.0]nona-2,5,8-triene (or its 2,4,8-triene isomer). However, the latter intermediate(s) could only be formed (with *cis* double bonds) in an allowed step *via* the folded conformation. Since this would not explain the different product stereochemistry observed for *cis*-bicyclo[6.1.0]nona-2,4,6-triene (or **1d** and **1e**) and the 9,9-dialkyl derivatives, we regard this pathway as unlikely in the case of the latter compounds.

(18) W. Grimme, cited in ref 2, footnote 12.

(19) We have already excluded the possibility of a multistep "symmetry allowed" route involving two 1,5-hydrogen migrations.<sup>1</sup> See also G. E. Petrowski, Ph.D. Thesis, University of California, Los Angeles, Calif., 1969 (in collaboration with S. Winstein) for similar experiments.

(20) A. G. Anastassiou, *J. Amer. Chem. Soc.*, **90**, 1527 (1968).

(21) A related but less explicit suggestion has been made by J. M. Holovka, P. D. Gardner, C. B. Strow, M. L. Hill, and T. V. Van Auken, *ibid.*, **90**, 5041 (1968).

Interestingly, **1d** rearranges to *cis*-8,9-dihydroindenes<sup>2,18</sup> (and therefore probably passes through an activated complex related to conformation **5**)<sup>1,22</sup> whereas **1a-c** do not. Apparently two alkyl groups at C<sub>9</sub> (rather than only a *syn*-9-alkyl group) are required to eliminate rearrangement *via* conformation **5** as the major process. Additional data are required in order to define the cause of this behavior but we suggest that there is greater steric hindrance which is less easily relieved (a "buttressing effect"<sup>23</sup>) in the case of **1a-c**. That is,  $\angle C_1C_9CH_3$  ( $\alpha$  in structure **1**) may be smaller in the dialkyl derivatives than in **1d** (*cf.*  $\angle CCC$  in neopentane (109.5°) and isobutane<sup>24</sup> (111.2°) and  $\angle C=CC$  in isobutylene<sup>25</sup> (122.4°) and propene<sup>26</sup> (124.3°)), and

(22) W. Grimme, *Chem. Ber.*, **100**, 113 (1967).

(23) For other examples of buttressing effects see (a) F. H. Westheimer in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley & Sons, Inc., New York, N. Y., 1956, Chapter 12; (b) J. P. Mazaleyrat and Z. Welvart, *Chem. Commun.*, 485 (1969), and references cited.

(24) D. R. Lide, Jr., *J. Chem. Phys.*, **33**, 1519 (1960).

(25) L. H. Scharpen and V. W. Laurie, *ibid.*, **39**, 1732 (1963).

(26) D. R. Lide, Jr., and D. Christensen, *ibid.*, **35**, 1374 (1961).

in addition, the force constant ( $\bar{\nu}$ ) for increasing  $\alpha$  is probably substantially greater in the case of **1a-c** relative to **1d**;  $k$  for  $\angle C_{sp^2}C_{sp^2}C_{sp^2}$  has been calculated to be 87% greater than that for  $\angle C_{sp^2}C_{sp^2}H$ <sup>27</sup> and  $k$  for  $\angle C_{sp^2}C_{sp^2}C_{sp^2}$  (or  $\angle C_{sp^2}C_{sp^2}C_{sp^2}$ ) has been taken to be 67% greater than that for  $\angle C_{sp^2}C_{sp^2}H$  (or  $\angle C_{sp^2}C_{sp^2}H$ ).<sup>28</sup>

**Acknowledgment.** We are grateful to the National Science Foundation for support of this work, and to Badische Anilin- und Soda-Fabrik AG for a gift of cyclooctatetraene.

(27) (a) J. H. Schachtschneider and R. G. Snyder, *Spectrochim. Acta*, **19**, 117 (1963); (b) see J. B. Hendrickson, *J. Amer. Chem. Soc.*, **89**, 7036 (1967), for a lucid discussion.

(28) N. L. Allinger, J. A. Hirsch, M. A. Miller, and I. J. Tyminski, *ibid.*, **90**, 5773 (1968).

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## Additions and Corrections

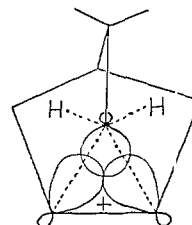
**Photolysis of 1,4-Dichlorobutane Sensitized by the  $n,\pi^*$  Singlet State of Acetone** [*J. Am. Chem. Soc.*, **91**, 4925 (1969)]. By MORTON A. GOLUB, Ames Research Center, National Aeronautics and Space Administration, Moffett Field, California 94035.

At the end of the caption for Figure 1,  $\Delta$  should be replaced by  $\triangle$ .

**Stable Carbonium Ions. LXXXVIII. Hydrogen-1 and Carbon-13 Nuclear Magnetic Resonance and Laser Raman Spectroscopic Study of the 2-Methyl-, 2-Ethyl-, and 2-Phenylnorbornyl Cation** [*J. Am. Chem. Soc.*, **91**, 3958 (1969)]. By GEORGE A. OLAH, JOHN R. DE-

MEMBER, CHRISTINE Y. LIU, and ANTHONY M. WHITE, Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106.

On page 3958, the figure was incorrectly reproduced. The corrected figure is shown below.



## Book Reviews

**The Chemistry of the Nitro and Nitroso Groups. Part I.** Edited by HENRY FEUER, Department of Chemistry, Purdue University, Lafayette, Indiana. Interscience Publishers, John Wiley and Sons, Inc., 605 Third Ave., New York, N. Y. 1969. xii + 771 pp. 16 x 23.5 cm. \$29.95.

There has not been a book on this subject before, notwithstanding the great technical as well as academic importance of nitro and nitroso compounds, and it can be judged that the appearance of such a book is overdue by the fact that this one requires two volumes (and even then is not encyclopedic). The subject is too large for proper coverage by one man, of course, and this first volume is written by ten different chemists in nine chapters.

The chapters cover not only classical, descriptive chemistry, but also photochemistry, spectroscopy (two chapters), and "theoretical

aspects of C-NO and C-NO<sub>2</sub> bonds." Some verge on the monumental (that on nitronic acids and esters has 138 pages and lists 490 references). The weakness of so many books consisting of contributed chapters—unevenness of presentation and coverage—is quite apparent, however. The chapter on theoretical aspects does not even mention the dimers of nitroso compounds and their intriguing structure, yet it discusses amine oxides and nitroxides, which are not really relevant to the book.

George Wright's chapter on the nitramino group stands out as particularly well written. It is critical, thorough, and includes both historical perspective and lots of usable information in tables. Arnold Nielsen's chapter on nitronic acids and esters shares honors with Wright's, and the two together make the book really worth having.