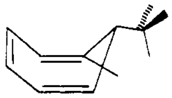
goes similar changes and exhibits two signals of unequal intensity at τ 8.03 and 8.06 (Figure 1B). Furthermore, at this temperature (−24°), two new signals appear: a doublet ($J = 9.1$ Hz) at τ 7.37 and a less intense broader doublet ($J = 7.7$ Hz) at τ 8.98 (7-methine protons; *vide infra*). The most reasonable interpretation of these results is that **2** exists as an equilibrating mixture of nonplanar conformers **2a** and **2b**, with one of these conformers in greater concentration.[11] Previous studies of cycloheptatriene systems have shown[1,2,5] that the *syn* or "axial" 7-proton is shielded[2] and therefore occurs upfield (τ 8.83–8.93) in comparison to the *anti*- or "equatorial" 7-proton (τ 6.67–6.99).[4b] From a consideration of the areas in the −24° spectrum of **2** (Figure 1B) and the relative positions of the 7-methine signals, we assign the resonances at τ 7.37, 8.06, and 9.23 to the 7-methine, 1-methyl, and 7-*t*-butyl protons, respectively, of conformer **2a**, and the signals at τ 9.08, 8.03, and 8.94 to the analogous protons of conformer **2b**. The striking conclusion is that **2a**, *the conformer with the "axial" 7-t-butyl group, is more stable.* This result is to be compared with the recent finding[5] that in 7-*t*-butylcycloheptatriene the "equatorial" conformer is more stable.

It should be noted that the chemical shift for the 7-methine proton in **2b** is 0.21 ppm higher than the value reported for 7-*t*-butylcycloheptatriene.[5] Furthermore, in **2b**, $J_{H_6-H_7}$ is somewhat higher than that reported for the analogous vincinal coupling in **1**.[2,5] These observations can be explained by noting that the *t*-butyl–methyl interaction in **2b** might cause the C_1–C_7–C_6 portion of the molecule to depart further than normal from the C_1–C_2–C_5–C_6 plane.[12] The net result would be greater shielding of the axial proton with a concurrent increase in the H–C_6–C_7–H dihedral angle, and hence in $J_{H_6-H_7}$.

The activation energy for the inversion process **2a** ⇄ **2b** was determined by comparing the line shapes of the *t*-butyl absorptions in the experimental spectra with those of theoretical spectra having various values of the mean lifetime (τ).[13,14] From the above treatment and an Arrhenius plot of the rate data, $E_a = 18.9 \pm 1.7$ kcal/mol[15] and $\log A = 15.4 \pm 1.3$, with the rate constant for the ring inversion at the coalescence temperature,[16] k_{28°, 58.8 sec^{-1}.

We note further, in a preliminary way, other interesting changes which occur in the spectrum of **2** at lower temperatures. Between approximately −45 to −80° the *t*-butyl resonance at τ 8.94 for the less stable conformer **2b** gradually broadens and then finally sharpens (at −104°) to three singlets of equal intensity at τ 8.78, 8.95, and 9.11 (Figure 1C). We ascribe these resonances to the three magnetically nonequivalent or anisochronous methyl groups in **2b** as depicted in **3**. To our knowledge, this is the first example of the direct nmr observation of three distinct methyl resonances for the *t*-butyl group in an organic molecule.[17] The thermodynamic parameters for these processes along with related studies are in progress and will be reported in further publications.



3

---

[11] We do not believe that the nmr spectral properties of **2** are indicative of a norcardiene. See E. Ciganek, *J. Am. Chem. Soc.*, **87**, 652, 1149 (1965).

[12] L. H. Knox, E. Velarde, and A. D. Cross, *ibid.*, **87**, 3727 (1965).

[13] The theoretical spectra were calculated using a FORTRAN IV coded program based on the equations of Gutowsky and Holm: H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956); for these calculations T_2 was determined from the average of the widths at half-height of the two *t*-butyl peaks under conditions of no exchange.

[14] C. A. Cupas, J. M. Bollinger, and M. Haslanger, *J. Am. Chem. Soc.*, **90**, 5502 (1968), and references therein cited.

[15] Errors reported are for the 90% confidence interval.

[16] T_c, the coalescence temperature, was taken as the temperature at which maximum broadening occurred.

[17] For examples where two signals of a *t*-butyl group are observed see F. A. L. Anet, M. St. Jacques, and G. N. Chmurny, *J. Am. Chem. Soc.*, **90**, 5243 (1968); J. P. N. Brewer, H. Heaney, and B. A. Marples, *Chem. Commun.*, 27 (1967).

[18] National Science Foundation Predoctoral Trainee, 1968–1969.

William E. Heyd,[18] Chris A. Cupas
Department of Chemistry, Case Western Reserve University
Cleveland, Ohio 44106

Received November 25, 1968

The Thermal Rearrangement of *anti*-9-Methyl-*cis*-bicyclo[6.1.0]nonatriene and *syn*-9-Methyl-*cis*-bicyclo[6.1.0]nonatriene

Sir:

The thermolysis of bicyclo[6.1.0]nona-2,4,6-triene at *ca.* 100° leads to a mixture of *cis*- and *trans*-8,9-dihydroindenes in a ratio of 9:1, respectively.[1-4] The stereochemical course of this reaction is not in accord with the prediction made by an orbital symmetry analysis for the concerted electrocyclic reaction.[5,6] Research conducted on the thermolysis of bicyclo[6.1.0]nona-2,4,6-trienes substituted at C_9 has resulted in the formation of substituted 8,9-dihydroindenes,[7,8] the stereochemistry of which provokes interesting questions with regard to the concerted or nonconcerted nature of this reaction.

We wish to report on the study of the thermolysis of *anti*-9-methyl-*cis*-bicyclo[6.1.0]nona-2,4,6-triene (**1**) and *syn*-9-methyl-*cis*-bicyclo[6.1.0]nona-2,4,6-triene[9] (**2**). The results of this study have important bearing on the mechanistic nature of this rearrangement.

The *syn* isomer **2** was readily available from a procedure developed by Katz.[9] The *anti* isomer was prepared from the alcohol[10] **3** by conversion to the tosylate **4** with tosyl chloride and pyridine, followed by reduction of **4** with lithium aluminum hydride to give **1**. The nmr spectrum of **1** was typical of bicyclo[6.1.0]nona-2,4,6-trienes, with the six vinyl protons at τ 4.2 (multiplet), three methyl protons plus two tertiary cyclopropyl protons at τ 7.8 (multiplet), and a tertiary cyclopropyl proton at τ 9.5 (multiplet).

---

[1] E. Vogel, *Angew. Chem.*, **73**, 548 (1961).

[2] E. Vogel, W. Wiederman, H. Kiefer, and W. Harrison, *Tetrahedron Letters*, 673 (1963).

[3] E. Vogel, W. Grimme, and E. Dinné, *ibid.*, 391 (1965); see footnote 8.

[4] W. Grimme, *Chem. Ber.*, **100**, 113 (1967).

[5] R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 395 (1965).

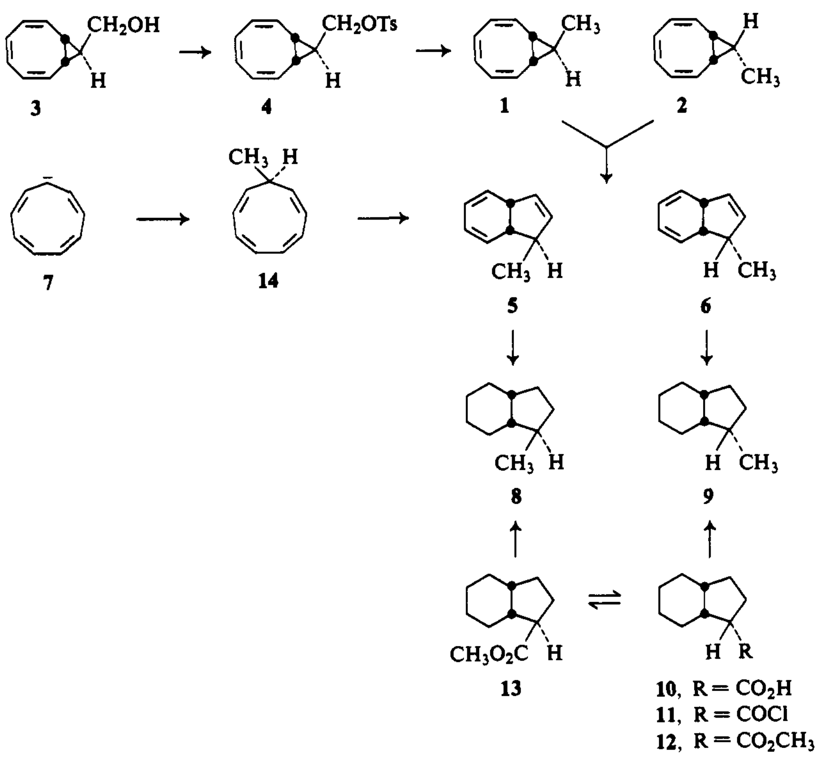
[6] H. C. Longuet-Higgens and E. W. Abrahamson, *ibid.*, **87**, 2046 (1965).

[7] K. F. Bangert and V. Boekelheide, *ibid.*, **86**, 905 (1964).

[8] G. J. Fonken and W. Moran, *Chem. Ind.* (London), 1841 (1963).

[9] T. J. Katz and P. J. Garratt, *J. Am. Chem. Soc.*, **86**, 4877 (1964).

[10] D. Phillips, *ibid.*, **77**, 5179 (1955); S. Akiyoshi and T. Matsuda, *ibid.*, **77**, 2476 (1955).



In separate experiments **1** and **2** were heated in the vapor phase under nitrogen, **1** at 170° for 50 min and **2** at 200° for 30 min. Analyses of the reaction mixture were made by vpc[11] and nmr. In both cases the same five-component mixture was produced; the major compounds (95% of the mixture) were **5** and **6**. In the case of **1** the ratio of **5**:**6** was 83:17 and in the case of **2** the ratio was 79:21.

The major products **5** and **6** were isolated by preparative vpc[11] and identified by their characteristic nmr spectra and by hydrogenation to **8** and **9** which were prepared by independent stereoselective synthesis.[12]

The nmr spectra of **5** and **6** were very similar, as each had six vinyl protons at τ 4.3 (multiplet), one bisallylic tertiary proton at τ 6.4 (doublet, $J = 12$ Hz), and two monoallylic tertiary protons at τ 7.4 (multiplet). The methyl group on **5** appeared at τ 8.90 (doublet, $J = 7$ Hz) and on **6** at τ 9.05 (doublet, $J = 7$ Hz).

The saturated derivatives **8** and **9** were independently prepared from 1-indenecarboxylic acid. This acid was reduced as previously described with hydrogen and Pt in acetic acid to give **10**.[13] Since the stereochemistry of the ring fusion had not been rigorously proven by previous workers[14] we degraded **10** to *cis*-hydrindan. This was accomplished by conversion of **10** to the acid chloride **11** with thionyl chloride, followed by reaction of **11** with *t*-butyl hydroperoxide in pyridine to give the *t*-butyl percarboxylate. Decomposition of the latter at 120° in cumene gave only *cis*-hydrindan. The acid chloride **11** was allowed to react with methanol to give **12**. The ester **12** had been shown by House[15] and by Fonken[8] to produce a mixture of **12**:**13** in a 15:85 ratio upon equilibration with sodium methoxide. By the above-described means we could obtain samples of **12** and **13** for conversion to **8** and **9**, respectively. This was done by reduction of **13** and **14** to **8** and **9** by the general sequence ester → alcohol → chloride → hydrocarbon.

We were also able to prepare the epimeric pair of *trans*-fused methylhydrindans (**15**). This was accomplished by reaction of *trans*-1-hydrindanone[16] with triphenylphosphonium methylide, followed by catalytic reduction with Raney nickel in ether at 1 atm, giving the epimeric mixture **15** in a ratio of *ca.* 60:40; no assignment of methyl group stereochemistry was made. When the five-component reaction mixture from thermolysis of **1** or **2** was hydrogenated and then compared by vpc and nmr with the independently prepared 1-methylhydrindans, **8**, **9**, and **15**, less than 0.1% **15** was found to be present and the major components were **8** and **9**. Assuming that no isomerization occurred during reduction there must have been no *trans*-8,9-dihydroindenes produced in the thermolysis.

These results indicate that when either **1** or **2** is thermally converted to **5** and **6** the reaction proceeds through a common intermediate in which the stereochemical integrity of the starting material is lost. The most likely choice for this intermediate is *cis,cis,cis,cis*-9-methylcyclononatetraene (**14**).

Since the reaction of lithium cyclononatetraenyl anion[17–19] (**7**) with methyl iodide must produce **14** as the

---

[11] The column used was 12 ft × $^{1}/_{8}$ in. 20% Apiezon L on Chromosorb W at 120°.

[12] In the course of preparing this manuscript we have learned from Dr. W. Grimme at the University of Cologne that he has made similar independent observations regarding the thermal rearrangement of **1** and **2** and these were presented at the Chemiedozenten-Tagung in Hamburg, April 3, 1968.

[13] W. S. Knowles, J. A. Kuck, and R. C. Elderfield, *J. Org. Chem.*, **7**, 374 (1942).

[14] The assignment of stereochemistry to **10** was made[8,15] on the basis that catalytic reduction should proceed mainly by *cis* addition and from the least hindered side. While this argument is reasonable and, *post hoc*, correct, it was essential to this problem to prove it rigorously.

[15] H. House and G. Frank, *J. Org. Chem.*, **30**, 3948 (1965).

[16] H. Brown and E. Negishi, *J. Am. Chem. Soc.*, **89**, 5477 (1967); we are very grateful to these authors for providing us with a sample of this ketone.

[17] T. Katz and P. Garratt, *ibid.*, **86**, 5194 (1964).

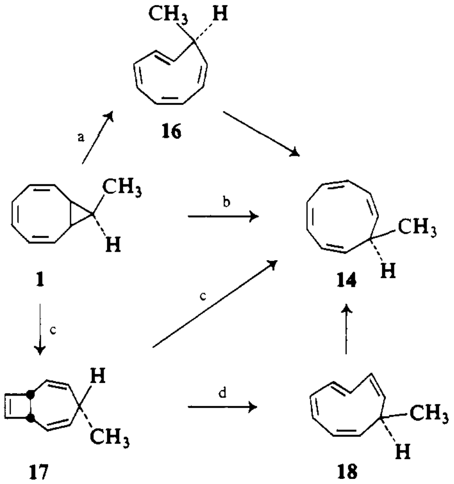
[18] E. LaLancette and R. Benson, *ibid.*, **87**, 1941 (1965).

[19] H. Simmons, D. Chestnut, and E. LaLancette, *ibid.*, **87**, 982 (1965).

initial product, this reaction provides a convenient test for the intermediacy of **14** in the thermal transformations described above. When the anion **7** in tetrahydrofuran was treated with methyl iodide at *ca.* 25°, vpc[11] and nmr analyses of the products of the reaction indicated that the same five products were produced as in the thermolysis of **1** or **2** and that the two major components, again about 95% of the mixture, were **5** and **6** in a ratio of 87:13, respectively.

These results clearly indicate that **14** is an important intermediate in the thermolysis of **1** or **2** and that the main products of the reactions, **5** and **6**, arise from **14** through a $6\pi \rightarrow 4\pi 2\sigma$ disrotatory electrocyclic reaction. In addition, these results show that the thermolysis of *cis*-bicyclo[6.1.0]nona-2,4,6-trienes substituted at C_9 is not a stereospecific reaction, as it might have previously been considered.[7,8] That is, the predominance of one isomer, *i.e.*, **5** over **6**, is due only to the stereoselectivity in the $6\pi \rightarrow 4\pi 2\sigma$ ring closure of **14** to these latter products.

In view of these results we suggest that there are four possible mechanisms for the transformation of **1** to **14**. They are (a) a conrotatory $6\pi 2\sigma \rightarrow 8\pi$ ring opening of **1** to give **16** followed by thermal *trans* → *cis* double isomerization; (b) a direct ring opening of **1** to give **14**; (c) a concerted [3.3] sigmatropic rearrangement of **1** to give **17** followed either by a nonconcerted ring opening to **14**; or (d) a conrotatory ring opening to **18** followed by a *trans–cis* double bond isomerization.



In view of the facts that *trans*-bicyclo[6.1.0]nona-2,4,6-triene is stable to 100° and polymerizes at higher temperatures,[20] that *trans–cis* double bond isomerizations probably have higher activation energy barriers than are required here, and that a good estimate, based on known models, for the activation energy for the nonconcerted **17** → **14** conversion is *ca.* 20 kcal/mol,[21] we prefer the **1** → **17** → **14** → **5** + **6** mechanism. However, we defer further discussion of this topic until current experiments are concluded.

Acknowledgment. We are pleased to acknowledge Professor William Okamura and Dr. William Rosen for helpful discussions and we are very grateful to Professor Herbert House for sending us spectra of his samples of **12** and **13**. In addition, acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Intramural Research Fund of the University of California for support of this research.

Phillip Radlick, William Fenical
Department of Chemistry, University of California
Riverside, California 92502

Received October 24, 1968

---

[20] S. Winstein and G. Petrowski, private communication.

[21] Made from data available for 1,2-divinylcyclobutanes.[22]

[22] H. M. Frey, *Advan. Phys. Org. Chem.*, 4, 176 (1966).

New Functional Halomethylmercury Compounds and Halocarbenes

Sir:

The recent disclosure of the low-yield, photolytic production of chlorocarbethoxycarbene, $ClCCO_2Et$, from ethyl chlorodiazoacetate[1] prompts us to report our own work concerning the generation of chloro- and bromocarbomethoxycarbenes, as well as of chloro(trifluoromethyl)carbene, by thermolysis of an appropriate organomercury precursor.

Phenyl(dichlorocarbomethoxymethyl)mercury, mp (with slow decomposition) 140–144°, and phenyl(dibromocarbomethoxymethyl)mercury, mp 154–156° dec, were prepared in good yield by the reaction shown in eq 1,

$$\mathrm{PhHgCl + Me_3COK + HCX_2CO_2Me \xrightarrow[-60\ \text{to}\ -50^\circ]{\text{THF}} PhHgCX_2CO_2Me + Me_3COH + KCl} \quad (1)$$

X = Cl, 75% yield
X = Br, 59% yield

using the general procedure we described recently for the synthesis of phenyl(trihalomethyl)mercurials in tetrahydrofuran medium.[2] Both mercurials appear to be good sources of the appropriate halocarbomethoxycarbene, although each is significantly more stable than its trihalomethyl analog, $PhHgCCl_3$ and $PhHgCBr_3$, respectively.

Transfer of $ClCCO_2Me$ was effected in 73% yield when 10 mmol of $PhHgCCl_2CO_2Me$, 38 mmol of cyclooctene, and 20 ml of chlorobenzene were heated at reflux under nitrogen for 11 days. (The progress of the reaction was followed by monitoring the consumption of the mercurial starting material by thin layer chromatography.[3]) The yield of phenylmercuric chloride was 91%. Both isomeric 9-chloro-9-carbomethoxybicyclo[6.1.0]nonanes were formed (in 1:3.5 ratio, in order of increasing retention time on a DC-200 silicone oil glpc column) (eq 2). The more abundant isomer had $n^{25}\mathrm{D}$ 1.4990. Phenyl(dibromocarbomethoxymethyl)mercury was found to be less stable thermally. In an analogous reaction with cyclooctene in chlorobenzene at reflux, phenylmercuric bromide was produced in 87% yield within 43 hr. The yield of the mixed 9-bromo-9-carbomethoxybicyclo[6.1.0]nonane isomers (bp 75–76° (0.03 mm); 1:2.3 ratio in order of increasing retention time on a silicone oil column) was 50%.

9-Chloro-9-carbomethoxybicyclo[4.1.0]heptane was not obtained when $PhHgCCl_2CO_2Me$ was treated with anhy-

---

[1] U. Schollkopf, F. Gerhart, M. Reetz, H. Frasnelli, and H. Schumacher, *Ann. Chem.*, **716**, 204 (1968).

[2] D. Seyferth and R. L. Lambert, Jr., *J. Organometal. Chem.*, **16**, 21 (1969).

[3] D. Seyferth and J. M. Burlitch, *ibid.*, 4, 127 (1965).,