Communications

Synthesis and Thermal Rearrangement of *exo*-Tetracyclo[4.3.0.0^{2,4}.0^{5,7}]non-8-ene, a σ-Homosemibullvalene. A Novel Entry into the C_9H_{10} Energy Manifold

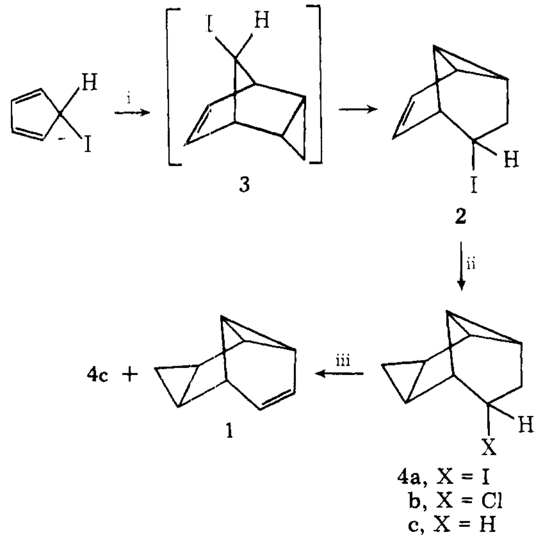
Summary: *exo*-Tetracyclo[4.3.0.0^{2,4}.0^{5,7}]non-8-ene (σ-homosemibullvalene, **1**) has been conveniently synthesized in two steps from the 5-iodocyclopenta-1,3-diene–cyclopropene cycloadduct and its thermal chemistry examined.

Sir: Recent interest in the chemistry and σ,π-isomerizations of σ-homobenzene[1] and σ-homotropilidene[2] derivatives, including fluxional behavior of the latter, has focused attention on further homologues related to these systems. We now report the synthesis and thermal rearrangement of the *cis*-σ-bishomotropilidene, *exo*-tetracyclo[4.3.0.0^{2,4}.0^{5,7}]non-8-ene (**1**), a σ-homosemibullvalene which unlike its next lower homologue, semibullvalene,[2b,c] is surprisingly resistant to thermal σ,π-valence isomerization.

Treatment of 5-iodocyclopenta-1,3-diene[3] with excess cyclopropene at −78 °C, followed by intermittent warming to 0 °C, afforded the tricyclooctenyl iodide **2** as a colorless oil in variable (40–90%) yield.[4] The structure and stereochemistry of **2** was readily established by its characteristic NMR spectrum that includes the expected doublet of doublets for the C-4 exo proton.[5] This one-step entry into the dihydrosemibullvalene ring system is most obviously a consequence of the facile rearrangement,[5,6] perhaps with thallium ion catalysis, of the initial (4 + 2) adduct, *anti*-8-tricyclo[3.2.1.0^{2,4}]oct-6-enyl iodide (**3**). Cyclopropanation of **2** (see Scheme I) gave in 90% yield the tetracyclic iodide **4a** [δ (CCl_4) 4.05 (ddd, 1 H), 1.0–3.1 (br m, 8 H), 0.55 (m, 1 H), 0.02 (m, 1 H); M^+ (70 eV) *m/e* 245.9895 (weak), 119 (66), 91 (100)].[7] The stereochemistry of the newly incorporated cyclopropane ring follows from the highly selective steric preference for exo cyclopropanation of norbornene type double bonds.[8]

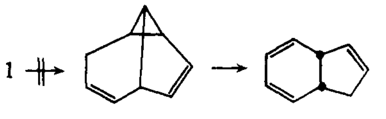
Quantitative conversion of **4a** to a 2:3 mixture of **1** and **4c**, respectively, was accomplished using a slight molar excess of KO-*t*-Bu in dimethylformamide at 110 °C for 2.5 h under nitrogen. The two-component mixture was cleanly separated by preparative GLC to yield the desired **1** [δ (CCl_4) 5.54 (m, 2 H), 3.25 (br d, 1 H), 0.9–2.1 (m, 5 H), −0.1–0.1 (m, 2 H); M^+ (70 eV) *m/e* 118 (40), 117 (100), 91 (40); $M^+ + 1$ (30 eV) 119.0817, M^+ 118.0766,[9] $M^+ - 1$ 117.0704][10] and its dihydro derivative **4c**. The structure of **4c** was confirmed by comparison with authentic material prepared by sodium metal reduction of **4a** in refluxing THF–*t*-BuOH).

Scheme I

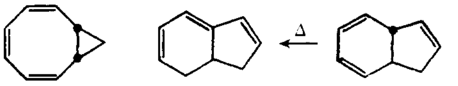


Reagents: i, c-C_3H_4, −78 to 0 °C; ii, CH_2N_2–CuCl, CH_2Cl_2; iii, KO-*t*-Bu–DMF, 110 °C.

At the outset investigation of the thermal behavior of **1** was largely prompted by consideration of its potential for homo-Cope rearrangement to the known[11] π-homosemibullvalene isomer **6**. Indeed a completely analogous 6π-electron reorganization has been recently proposed to account for the rearrangement and eventual fragmentation of a pentacyclic $(CH)_{12}$ hydrocarbon.[12] Initial thermolysis studies of **1** indicated complete recovery after heating in a static system at 140–150 °C for 12.5 h. On the basis of the reasonable assumption that the isomerization **1** → **6** is exoergic and assuming <10% conversion to the π isomer at these temperatures, the activation energy (E_a) for the homo-Cope rearrangement of **1** is estimated to be >35 kcal/mol, a value at least 30 kcal/mol higher than the similar activation barrier for the degenerate Cope rearrangement in semibullvalene.[2c]



On pyrolysis in a glass packed Vycor tube flow system (10 Torr, N_2; contact time ~1 s) at 400–520 °C **1** undergoes rearrangement to a mixture of hydrocarbons reminiscent of that obtained from the thermolysis of other isomeric C_9H_{10} systems,[11,13,14] most notably bicyclo[6.1.0]nona-2,4,6-triene (**7**),[13] with one significant difference. Thus at 520 °C **1** was converted (99.2%) to a six or seven component mixture of hydrocarbons, the major components of which were identified as 7,7a-dihydroindene (**8**; 55.2%),[15] indane (21.2%), indene (6%), and *cis*-3a,7a-dihydroindene (**9**; 10–12%).[16] Analogy to the previously reported[13d,f,g] interconversions of alkylated dihydroindene isomers suggested that **8** must arise by 1,5-sigmatropic isomerization of *trans*-3a,7a-dihydroindene (**10**). Indeed pyrolysis of an enriched sample of **10** (77.8% **10**, 18.1% **8**)[17] under the identical conditions (520 °C, 10 Torr, N_2) afforded a similar product distribution to that obtained from **1**.[18] By contrast *cis*-dihydroindene **9** was largely (>97%) unaffected by these flow pyrolysis conditions.



The striking conclusion from the above results is that thermal isomerization of **1** leads to predominantly *trans*- rather than *cis*-dihydroindene, which is the customary molecular sink for thermal isomerizations of C_9H_{10} systems.[14] Therefore substantial rearrangement by the homo-Cope pathway is ruled out since **6** has been previously shown[11] to rearrange quantitatively to *cis*-dihydroindene **9**. The most plausible precursor to **10** is either *cis*,[3] *trans*- or *cis*,[2] *trans*,-

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cis-cyclonona-1,3,5,7-tetraene (or both). Both of these highly reactive tetraenes have been implicated as intermediates, along with the all *cis*-cyclononatetraene, in the thermal isomerization of the bicyclononatriene **7**, although the mode of their formation is still a matter of conjecture.[13] It is clear, however, that **7**, in its normal state, cannot be an intermediate in the isomerization of **1**, since under the above flow pyrolysis conditions it gave, as expected, *cis*-dihydroindene **9** as the major (80%) thermal product.

While further mechanistic studies are required we would suggest the intriguing possibility of retro Diels–Alder cleavage of **1** to vibrationally excited **7** in its extended conformation, which thereupon suffers immediate symmetry-allowed electrocyclic opening to *cis*,[3] *trans*-cyclononatriene.[19]

References and Notes

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(4) The yield of **2** appeared to be enhanced when a slight excess of thallium cyclopentadienide was used in the preparation of 5-iodocyclopenta-1,3-diene.

(5) K. Henrick and B. L. Johnson, *Aust. J. Chem.,* **25,** 2263 (1972); see also J. S. Haywood-Farmer and R. E. Pincock, *J. Am. Chem. Soc.,* **91,** 3020 (1969), and C. L. Deyrup, Ph.D. Dissertation, Boston University, 1970.

(6) H. Tanida, T. Tsuji, and T. Irie, *J. Am. Chem. Soc.,* **89,** 1953 (1967); M. A. Battiste, C. L. Deyrup, R. E. Pincock, and J. Haywood-Farmer, *ibid.,* **89,** 1954 (1967).

(7) A low intensity ion in the mass spectrum of **4a** at *m/e* 154 was attributed to trace contamination by chloride **4b,** presumably formed through halide exchange with the catalyst CuCl.

(8) Cf. J. Haywood-Farmer, R. E. Pincock, and J. I. Wells, *Tetrahedron,* **22,** 2007 (1966); M. A. Battiste and M. E. Brennan, *Tetrahedron Lett.,* 5857 (1966).

(9) The measured parent ion (M^+) mass is slightly beyond acceptable error limits due to interference by the ^{13}C isotope peak of the intense (base) $M^+ - 1$ ion; however, the flanking *m/e* 119 and 117 ions gave the correct accurate masses for the assigned structure.

(10) After the studies reported in this paper were concluded our attention was directed to a report by T. Kumagai and T. Mukai [*Chem. Lett.,* 1187 (1975)] in which these authors propose the structure **1** for the 30% component isolated from the acetone-sensitized photolysis of tricyclo[3.2.2.$0^{2,4}$]-nona-6,8-diene (homobarrelene). Structure assignment by the Japanese workers was largely based on analysis of the NMR (100 MHz) spectrum, which we find to be essentially identical with the spectrum (60 MHz, briefly annotated in the text) of our synthetic material, thus confirming their assignment.

(11) J. A. Berson, R. B. Boettcher, and J. J. Vollmer, *J. Am. Chem. Soc.,* **93,** 1540 (1971).

(12) E. Vedejs and R. A. Shepherd, *J. Org. Chem.,* **41,** 742 (1976).

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(14) For a brief summary of the thermal isomerizations of a variety of C_9H_{10} systems, see J. M. Brown, *MTP Int. Rev. Sci.: Org. Chem., Ser. One,* **5,** 196–200 (1973).

(15) To our knowledge **8** has not been previously reported. Its identity follows from its NMR [($CDCl_3$) complex multiplets from δ 1.6–3.0 (allylic) and 5.5–6.4 (vinyl) in 1:1 area ratio] and UV [λ_{max} (CCl_4) 300 nm (ϵ 8000)] spectra, its extreme sensitivity to oxygen and partial conversion to indene on exposure to air, and its alternative generation on pyrolysis of **10.** In addition, the vinyl proton pattern in the NMR spectrum of **8** is essentially identical with that for 1,1-dimethyl-7,7a-dihydroindene.[13d] We thank Professor S. W. Staley for copies of the NMR and IR spectra of the latter hydrocarbon taken from the Ph.D. Thesis of T. J. Henry, University of Maryland, 1971. Indane and indene were identified by preparative GLC isolation and comparison of NMR spectra with those of authentic samples.

(16) Allylbenzene, an anticipated secondary pyrolysis product, was also detected by NMR as a minor product, but was inseparable from *cis*-dihydroindene **9** under the capillary GLC conditions utilized for product analysis. In a later run NMR analysis of the *cis*-dihydroindene component after preparative GLC collection showed <10% contamination by allylbenzene.

(17) The enriched sample of *trans*-dihydroindene **10** was secured by preparative GLC collection of the minor (15%) dihydroindene isomer obtained on pyrolysis of **7** at 75 °C. Under the GLC conditions **10** is partially isomerized to **8.**

(18) One difference noted in the pyrolysis of **10** is that the relative yield of *cis*-dihydroindene **9** is considerably reduced (<5%). We estimate the allylbenzene/**9** ratio in this case to be essentially equal from NMR analysis of the crude pyrolysis mixture.

(19) We wish to thank the National Science Foundation for financial support of this work (Grant GP-38630X) and Dr. Roy King for his assistance with the aquisition and interpretation of the mass spectrometric data.

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Received September 13, 1977

Aryl Selenocyanates and Aryl Thiocyanates: Reagents for the Preparation of Activated Esters

Summary: Treatment of carboxylic acids with phenyl selenocyanate and phenyl thiocyanate in the presence of tri-*n*-butylphosphine affords benzeneselenol esters and benzenethiol esters, respectively.

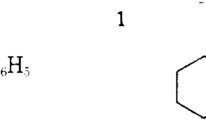
Sir: As a result of current interest in the synthesis of naturally occurring macrocyclic lactones and lactams,[1] considerable attention has been focused on the preparation of activated esters.[2,6] We wish to report a new method for the preparation of selenol esters (eq 1) and thiol esters (eq 2) which proceeds

$$\mathrm{RCOOH} \xrightarrow[\substack{\mathrm{Bu_3P} \\ \mathrm{CH_2Cl_2}}]{\mathrm{ArSeCN}} \mathrm{RCOSeAr} \qquad (1)$$

$$\mathrm{RCOOH} \xrightarrow[\substack{\mathrm{Bu_3P} \\ \mathrm{CH_2Cl_2}}]{\mathrm{ArSCHN}} \mathrm{RCOSAr} \qquad (2)$$

under mild conditions. During the course of examining the reaction of aryl selenocyanates with alcohols[7] and aldehydes,[8] we observed that carboxylic acids dissolved in methylene chloride or tetrahydrofuran reacted with aryl selenocyanates in the presence of tri-*n*-butylphosphine. We also demonstrated that substitution of aryl thiocyanates for aryl selenocyanates results in the formation of thiol esters.

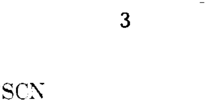
In the case of selenol esters, the reaction is best carried out employing 1.0 equiv of aryl selenocyanate and 2.0 equiv of tri-*n*-butylphosphine. The reaction can be performed on a variety of alkyl and aryl carboxylic acids (Table I) employing phenyl selenocyanate.[9] Cyclohexanecarboxylic acid, upon treatment with phenyl selenocyanate and tri-*n*-butylphosphine in methylene chloride, gave rise to an 88% yield of pure activated ester. Yields of pure isolated benzeneselenol esters are generally high (Table I). Reaction of *p*-chlorobenzoic acid with phenyl selenocyanate under the conditions described above gave rise to only a 36% yield of product, with the major product (54%) being diphenyl diselenide. Utilization of *o*-



1

$BrCH_2(CH_2)_5COSC_6H_5$

2



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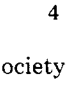

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