

close to that observed in ordinary donor-acceptor complexes.¹² The lesser broadening of 1-CH₃ relative to 8-CH₃ and the broadening of a vinyl α -H¹⁸ can yield detailed information on how the pyrroles I and IV aromatic skeletons actually overlap.

The stereospecific dimer formation suggests that the four pyrroles in protoporphyrin IX differ significantly in their donor or acceptor capabilities, with I the best donor and IV the best acceptor.¹⁹ These differential donor-acceptor capabilities of the individual pyrroles may be crucial for efficient porphyrin-protein linkages in hemoproteins.¹⁻⁴

A detailed study of this dimerization in a variety of porphyrin derivatives in several solvents is in progress and will be reported in the near future. The relevance of the dimerization to the interpretation²⁰ of the methyl shifts in low-spin hemes and hemoproteins will be discussed in detail elsewhere.

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- Spectra were recorded on a Jeol PS-100 FTNMR spectrometer, equipped with a Digilab NMR-3 data system; 19 μ sec 90° pulse widths were used for 25 scans on 0.05 M and 200 scans on 0.005 M solutions.
- The authors are indebted to M. P. Klein, University of California, Berkeley, for 220-MHz proton spectra.
- The estimated separation from the relaxation data depends on the degree of association. We cannot exclude higher aggregates than dimers at this time. Higher aggregates would still require the stereospecific stacking indicated in D of Figure 1.
- The broadening of the downfield vinyl α -H peak identifies it as 2-vinyl. The differential broadening of 1-CH₃ and 8-CH₃, in addition to the broadening of 2- α -vinyl-H but *not* 7- α -CH₂, must reflect some asymmetry in the overlap of the I and IV pyrroles.
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Tricyclo[2.2.0.0^{2,6}]hexan-3-one

Sir:

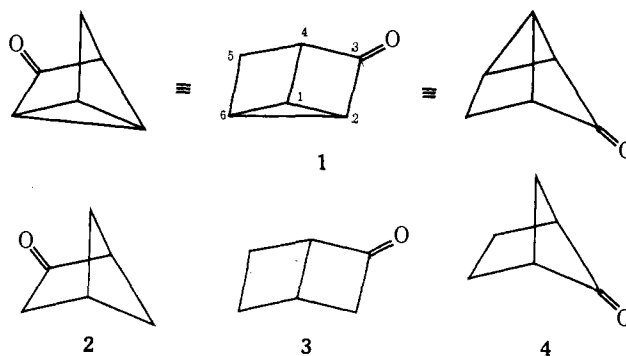
The chemistry of highly strained small ring compounds continues to be of great interest. We report here the synthe-

Table I. Pmr (220 MHz) Assignments to 1^a

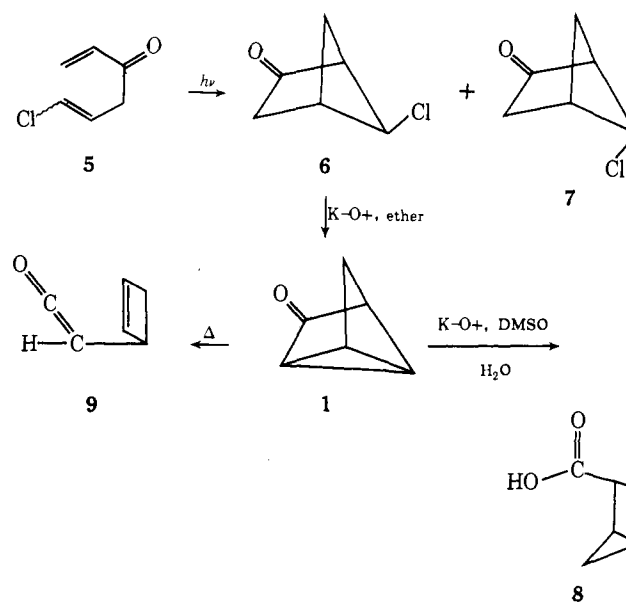
| Assignment | δ (shape) | Coupling constants (Hz) |
|-----------------------|------------------|--|
| H ₁ | 3.58 q (broad) | $J_{1-4} = 4$, $J_{1-5}(\text{endo}) = 4.5$, $J_{1-6} = 3.8$ |
| H ₂ | 2.88 d of d | $J_{2-6} = 10$, $J_{2-4} = 4$ |
| H ₄ | 2.70 q | $J_{4-1} = J_{4-2} = J_{4-3} = 4$ |
| H ₅ (exo) | 2.78 m | $J_{5-4} = 4$, $J_{5-5'} = \pm 7.5$, $J_{5-6} = 3.5$ |
| H ₅ (endo) | 1.91 d of d | $J_{5'-1} = 4.5$, $J_{5'-5} = \pm 7.5$ |
| H ₆ | 2.46 m | $J_{6-1} = 3.8$, $J_{6-2} = 10$, $J_{6-5} = 3.5$ |

^a Eu(Fod)₃ titration studies showed that the 2.70 and 2.88 patterns shifted most dramatically, the 1.91 and 3.58 peaks an intermediate amount, and the 2.46 and 2.78 peaks the least.

sis and structure proof of the title compound **1**, a derivative of a rare ring system.^{1,2} With the preparation of **1**, ring functionalized derivatives of the simple tricyclo[2.2.0.0^{2,6}]hexane system become available for the first time. Ketone **1** is formally a dehydro derivative of the already strained ketones bicyclo[2.1.1]hexan-2-one³ (**2**), bicyclo[2.2.0]hexan-2-one⁴ (**3**), and bicyclo[2.1.1]hexan-5-one⁵ (**4**).



Photolysis of a cis-trans mixture of 6-chlorohexa-1,5-dien-3-one^{6,8} (**5**) affords an approximately 1:1 mixture⁹ of *exo*-5-chlorobicyclo[2.1.1]hexan-2-one (**6**) and its *endo* isomer **7**. Treatment of the *exo* isomer **6** with potassium *tert*-butoxide in ether at 0°, followed by rapid work-up in the cold, affords **1** in about 80% yield. Purification by glpc at temperatures below 50° removes final traces of *tert*-butyl alcohol. Thermal rearrangement to **9** occurs readily at higher temperatures.



Tricyclo[2.2.0.0^{2,6}]hexan-3-one (**1**) has the nmr spectrum reported in Table I. Assignments were made by comparison with nortricyclanone,¹¹ Eu(Fod)₃ shift reagent

studies, and decoupling experiments. The infrared spectrum (CCl_4) has significant absorption at 3060, 3030, 2950, 2870, 1775, and 1759 cm^{-1} . The doublet carbonyl band is similar to that observed in nortricyclanone (1768 and 1755 cm^{-1}).¹² The mass spectrum of **1** shows the molecular ion as the parent peak at m/e 94, and only two other peaks with intensity over 10% at m/e 66 (31%) and m/e 65 (25%). The ultraviolet spectrum (cyclohexane) has λ_{max} at 254 $m\mu$ (ϵ 30).

The structure of **1** was proven chemically by cleavage¹³ with potassium *tert*-butoxide in dimethyl sulfoxide–water to give in high yield the known¹⁴ *endo*-bicyclo[2.1.0]pentane-2-carboxylic acid (**8**).

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- (8) All new compounds except **9** gave satisfactory spectral and combustion analysis data. Compound **9** was converted into characterized derivatives.
- (9) As expected,¹⁰ the composition of the mixture is independent of the isomeric ratio of enone **5**.
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Competitive Dissociation and Rearrangements of 1,5-Hexadiene¹

Sir:

The complete elucidation of a reaction mechanism, like that of a molecular structure, first requires a complete list of alternative possibilities. One or more of these can then be excluded, most often by successive appropriately designed experiments, until the correct one is revealed. Trivial as this logical prerequisite might appear, it has only recently been made explicit.²

For example, the pioneering stereochemical analysis of the Cope rearrangement³ is now recognized to have been both ambiguous and incomplete. It was ambiguous because the experimental data agreed equally well with a twist transition state as they did with a chair (Figure 1).^{2b,4} It was incomplete because an appropriately labeled precursor (and 11 kcal/mol more in activation enthalpy) subsequently revealed a second rearrangement mechanism—perhaps the boat or the plane.⁵

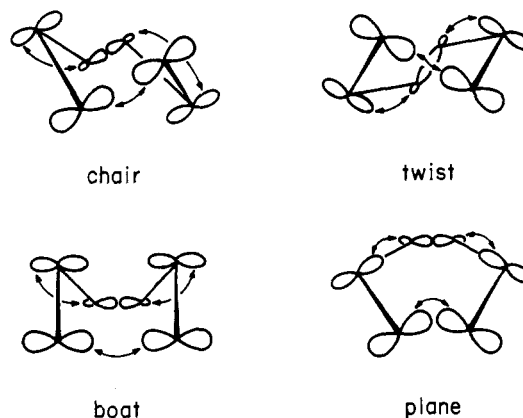


Figure 1. The symmetry-allowed [3,3]sigmatropic transition states—supra-supra (chair and boat) and antara-antara (twist and plane).^{2b}

The data, then available, could not distinguish these latter two alternative [3,3]sigmatropic possibilities. Neither could they exclude any of four [1,3]sigmatropic mechanisms. To confound matters still further, several critical colleagues have since expressed the view that yet another possibility—homolytic dissociation to allyl free radicals—had prematurely been rejected. Empirical generalizations^{6a} and/or extrapolation from higher temperature data^{6b} suggest homolytic rate constants which fall dangerously close to those that were observed.^{2b}

We are therefore particularly pleased to report new experimental results that exclude both the [1,3]sigmatropic and the dissociative possibilities. In this way, the higher temperature Cope rearrangement is now rigorously restricted to being either the boat or the plane—a level of ambiguity which still characterizes the first discovered, lower temperature process.^{3,4}

1,5-Hexadiene-*d*₂, the 1:1 mixture of 1*Z*, 6*E* and 3*R*, 4*S* isomers obtained by pyrolysis of *exo*-bicyclo[2.2.0]hexane-2,3-*d*₂⁷ at 207°, served as starting material for each of two different approaches. In the first (a classical⁹ crossover experiment), it was diluted with an equal quantity of undeuterated diene and pyrolyzed at ~600 Torr and 282° for 48 hr (2.0 half-lives of the higher temperature rearrangement). Diimide reduction, followed by mass spectrometric analysis of the resulting *n*-hexanes, provided results that were indistinguishable from the 1:1 superposition of identically obtained data but from *separate* dideuterated and undeuterated samples.¹⁰

Unambiguous in excluding dissociation to allyl radicals, such data are less suited to more quantitative scrutiny. Neither can they distinguish the [1,3]- from the [3,3]sigmatropic possibilities. Both reservations are satisfied by the alternative approach, one that was explicitly suggested by the rigorous analysis of tetradeuterio- and dideuterio-1,5-hexadiene rearrangement possibilities.¹¹

As illustration, oxidative degradation of equilibrating 1,6- and 3,4-dideuterio-1,5-hexadienes provides succinic-*d*₁ acid only to the degree that [1,3]sigmatropy competes with [3,3] (Scheme I). (Here and subsequently, closed circles label a monodeuterated carbon.)

In algebraic detail, the linear analysis of labeling experiments approach^{2b} subjects each of the ten accessible dideuterio-1,5-hexadienes to the operation of nine possible reaction mechanisms: all five [3,3]sigmatropics (of rate constants k_C , k_T , k_B , k_P , and k_A) and all four [1,3]sigmatropics (of rate constants k_V , k_S , k_H , and k_D). Symmetrization¹² and symmetry-assisted diagonalization¹³ of the mechanism matrix generates the ten equations (eq 1):

$$\chi_i = \chi_i(0)e^{-\lambda_i t} \quad (1)$$