POPULATION ANALYSIS OF 2,8-PENTAMETHYLENESEMIBULLVALENE. DIRECT

OBSERVATION OF INDIVIDUAL NONDEGENERATE VALENCE ISOMERS

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The exceedingly low activation energy (calculated: 2.3-3.6 kcal/mol[1]) associated with

the degenerate symmetry-allowed [3,3]sigmatropic shift in semibullvalene effectively precludes

the observation of temperature-dependent pmr spectra down to -110°.[2] With octamethylsemi-

bullvalene, slow-exchange pmr spectra have been obtained (-151°) since exhaustive

methyl substitution of the ring system serves to increase the free energy of activation of the

Cope rearrangement to 6.4 kcal/mol.[3] With the recent successful synthesis of a number of

2,8-bridged semibullvalenes (e.g., 1-3),[4] there have arisen a number of ancillary considerations

concerned with such matters as changes in equilibrium position with modification of the annela-

ted ring,[4,5] effects arising from purely inductive contributions of the alkyl and alkenyl

chains,[1b,6] variations in the activation energies of the sigmatropic rearrangement with alter-

ation of bridge size, and the like.

Hydrocarbons 1 and 2 are not particularly amenable to a study of changes in tautomeric

equilibrium with temperature, because at 40° the respective K_{eq}'s are already weighted heavily

in the directions indicated. Further perturbations of the ground state equilibria with chang-

ing T would prove too small to measure accurately in these cases. The pentamethylene bridged

analog 3, in contrast, exists as a more equitable distribution of valence isomers 3a and 3b,[5]

and the molecule readily accommodates determination of the free energy of activation for the

Cope rearrangement. Additionally, the present study records the first instance in which di-

rect observation of two nondegenerate semibullvalene isomers has proven possible.

The pmr spectrum of 3 at fast exchange (Figure 1, -27°) consists of a doublet at δ 5.08

from the permanently olefinic protons (H_a-H_a'), a triplet at 4.37 from the protons that exchange

between olefinic and tertiary cyclopropyl positions (H_b-H_b'), a doublet of triplets centered

at 3.09 from H_c-H_c', and a doublet at 2.77 from H_d-H_d'. The methylene protons (H_α, H_β, H_γ, and
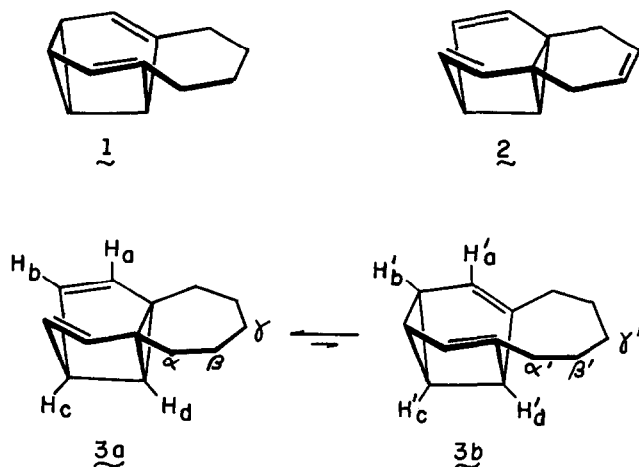
their primed counterparts) provide the envelope at 1.4-2.0, although half of the diastereo-

topic H_α-H_α' protons are probably responsible for the multiplet centered at 2.6. As the temp-

erature is lowered, the first spectral perturbation due to the Cope rearrangement ($3a \rightleftharpoons 3b$)

is a movement of lines that results from a shift in the equilibrium. This phenomenon is most

evident in the H_b-H_b' resonance, which shifts from 4.37 at -27° to 4.53 at -51°. As the temp-

erature is decreased further, the rate of the Cope rearrangement becomes slower than the pmr

time scale, with each resonance responding according to its slow-exchange chemical shift dif-

ference. Because of the large structural difference between H_b and H_b' their average resonance

broadens at the highest temperature, passes through coalescence at -85.5°, and separates into

distinct H_b (5.59) and H_b' (upfield shoulder at 2.34) peaks at -120°. The olefinic proton

absorption responds at a lower temperature to give separate slow-exchange peaks for H_a

(5.19) and H_a' (4.94). The H_c resonance reappears at slightly lower field (3.23),

and the H_d resonance at slightly higher field (2.62), superimposed on top of two H_α absorp-

tions. The H_c' and H_d' resonances are not distinguished. The methylene resonances undergo

alterations of peripheral interest with a clear slow-exchange limit at -120°. Designation

of the various resonances clearly shows that the more populous isomer is 3a. Direct integra-

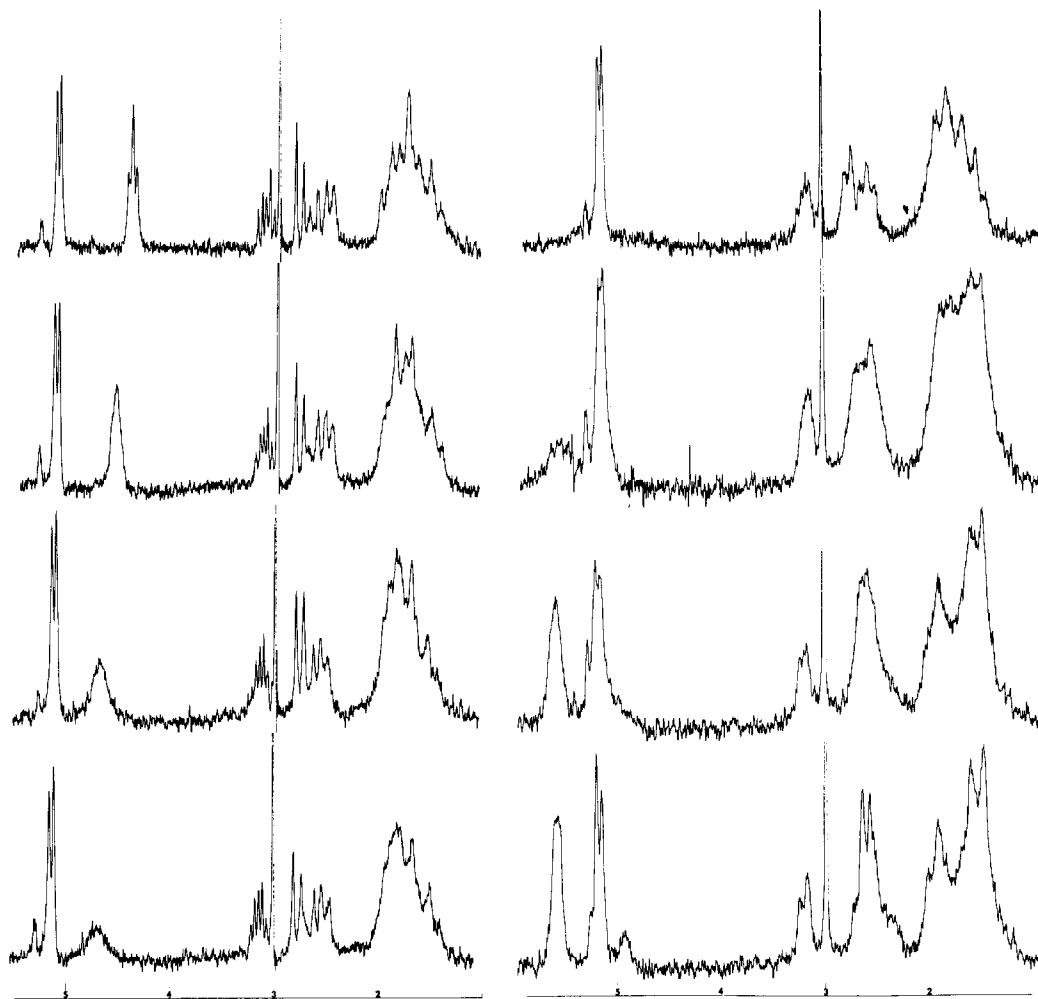tion of the H_a and H_a' peaks denotes that at -120°, there is 84% of isomer 3a and 16% of 3b,

Figure 1.   The proton magnetic resonance spectrum of pentamethylenesemibullvalene as a func-
            tion of temperature in CF_2Cl_2/CD_2Cl_2.   The temperatures for the left column from
            the top are -27, -51, -66, and -71°.   The temperatures for the right column from
            the top are -85.5, -100, -110, and -120°.   A small impurity resonance is present
            at δ 5.3, and a sharp impurity resonance at 3.0; these peaks were temperature in-
            dependent.

corresponding to a $\Delta \underline{G}°$ of 505 cal/mol.   It is noteworthy that the weighted-average (84/16)

position of the H_b and H_b' peaks does not correspond to the location of the observed peak at

higher temperatures, because of the strong temperature dependence of the equilibrium constant.

In order to reproduce the observed positions, a ratio of 76/24 is necessary at -85.5° (the

coalescence temperature) and of 62/38 at -27°.   With knowledge of the slow-exchange H_b and H_b'

chemical shifts ($\Delta\nu$ = 290.6 Hz) and the isomer populations (K_{eq} = 3.17), the free energy of activation was determined by complete lineshape analysis at the coalescence temperature (-85.5°) to be 8.9 kcal/mol (3a to 3b) or 8.5 kcal/mol (3b to 3a).

The dominance of 3a in the equilibrium mixture deviates from the established preference of alkyl groups for bonding to sp^2 rather than sp$^{2\cdot25}$- hybridized carbon in structurally related homotropilidenes.[7] It is obvious that the lesser annelation strain in 3 relative to 1 is not exploited in such a manner as to reveal itself by weighting in the 3b direction. Perhaps more important than electronic effects in this case is the partial release of nonbonded repulsions associated with the 1,3-dimethylenecyclooctane part structure in 3b. Thus, 3 provides an example of the caution which must be exercised in equating a diminution in ''bracketing strain'' with direction of equilibrium.

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