Equilibrium Displacements Resulting from Substitution of the Semibullvalene Nucleus

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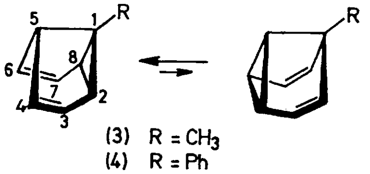
Summary To assess electronic effects on the very rapid semibullvalene valence isomerization process, a number of substituted derivatives of this hydrocarbon has been synthesized and the resulting perturbational effects on the individual equilibria evaluated by ^1H n.m.r.

SEMIEMPIRICAL MO calculations on substituent effects on cyclopropane rings involved in Cope rearrangements predict that electron-withdrawing groups will exert a stabilizing influence whereas donor substituents will be destabilizing.[1] These conclusions are supported by the rather large equilibrium displacements observed for cycloheptatriene–norcaradiene[2] and bullvalene[3] valence isomerizations. As noted by Schleyer,[4] however, these systems lack ideality owing to the heavily weighted ground-state preference for one of the constituent isomers. Two-fold degenerate systems are without this inherent structural disadvantage and consequently warrant detailed investigation of perturbational effects arising from framework substitution. Because the activation energy for Cope rearrangement in semibullvalene is the lowest on record,[1,5] we have prepared a number of substituted semibullvalenes by recently developed methods[6] and now report on their valence tautomerism.

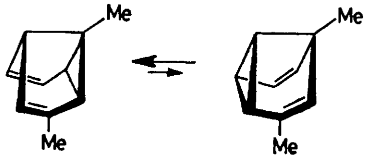
(1) (2)

Bridge	Mole fraction (40 °C) (1)	(2)	Δ°*G* cal/mol
a; X = CH_2	57	43	175
b; X = $\overset{cis}{\mathrm{CH = CH}}$ ..	74	26	650
c; X = CH_2CH_2	10	90	−1360
d; X = $CH_2CH_2CH_2$ ..	42	58	− 200

The series of 2,8-annelated semibullvalenes (**1**) ⇌ (**2**)[7] revealed a dominance of (**2c**) and (**2d**) at equilibrium (40°), in agreement with the known preference of alkyl groups for attachment to double bonds.[3,8] However, the assumedly[9] lesser bridging strain in (**1d**) ⇌ (**2d**) does not reveal itself by excessive preference for (**2d**).† Monosubstituted semibullvalenyl systems are so constructed that steric influences at differing ring positions should be minimal and accordingly contribute little to the ground-state energy profiles. With but two exceptions,[5b,7] the activation energies of semibullvalene interconversions have proven too low to permit slowing of rearrangement on the ^1H n.m.r. time scale, and we encountered comparable difficulties. However, the preferred equilibrium displacements were easily recognized by other ^1H n.m.r. features.



(3) R = CH_3
(4) R = Ph
(5) R = CH_2OMe



(6)

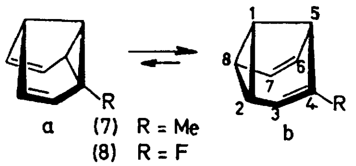
Compounds (**3**)—(**5**) were prepared in several steps by bond reorganization of the corresponding functionalized cyclo-octatetraenes and (**6**) was obtained from 1-methyl-*cis*-bicyclo[3,3,0]octane-3,7-dione. Analysis of the 60 and 100 MHz spectra of these 1-substituted semibullvalenes in the temperature range +40 to −120° revealed the positional preference in all cases to be that with attachment of R to the cyclopropane ring. Double resonance techniques were used to measure spin–spin interactions and confirm the ordering of protons in the dominant structure. In the case of (**3**), for example, the permanently olefinic protons 3- and 7-H are seen as a dd ($J_{3,4} = J_{6,7} = 4{\cdot}0$ Hz, $J_{2,3} = J_{7,8} = 2{\cdot}0$ Hz) centred at δ 5·06 (+36°; CS_2 solution). The proton pairs 2- and 8-H (δ 3·42, m) and 4- and 6-H (δ 4·78, dd) prove distinguishable since only the latter are coupled to 5-H (δ 2·68, t, $J_{4,5} = J_{5,6} = 3{\cdot}0$ Hz). The appearance of 4- and 6-H at substantially lower field than 2- and 8-H demands that the equilibrium lie significantly to the left. The other three compounds show comparable spectral features.‡

Equilibrium data were also obtained for compounds (**7**)—(**9**) by ^1H n.m.r. methods. Although less symmetrical than compounds (**3**)—(**5**), these 2-substituted semibullvalenes show a preference for attachment of the R group to olefinic carbon such that simple integration techniques could be used. The ^1H n.m.r. spectrum of (**8**) at +35° in CS_2, for example, shows δ 2·84br (3 × pseudo-cyclopropyl-H), 3·17 (m, 5-H), 4·62 (1H, m, 3-H), and 5·41 (2H, m,

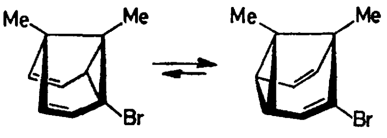
† Under conditions of slow exchange, 4- and 6-H of (**1d**) and (**2d**) appear at δ 5·59 and 2·34, respectively. These chemical shifts establish the approximate limits for all 4- and 6- protons in the 2,8-annelated semibullvalene series and thus allow approximate calculation of the mole fractions through use of the following equation (L. A. Paquette, S. Kirschner, and J. R. Malpass, *J. Amer. Chem. Soc.*, 1970, **92**, 4330): $\rho = (\delta_m - \delta_c)/(\delta_v - \delta_c)$ where δ_m = time average absorption of 4- and 6-H, $\delta_c = 2{\cdot}34$, and $\delta_v = 5{\cdot}59$.

‡ *E.g.* ^1H n.m.r. data for (**4**): δ (CD_2Cl_2; Me_4Si; +33°) 7·10 (5H, m), 5·43 (m, 4-and 6-H), 5·21 (m, 3- and 7-H), 3·43 (m, 2- and 8-H), and 3·31 (t, $J_{4,5}$ 2·5 Hz, 5-H).

6- and 7-H). Similar results were obtained for (**7**), (**9**),§ and the somewhat more structurally encumbered (**10**).[10]



(**7**) R = Me
(**8**) R = F
(**9**) R = CH$_2$OMe



(**10**)

The preference of various substituents for bonding to olefinic > cyclopropyl > aliphatic is clearly demonstrated. Our results with (**3**) and (**7**) compare favourably with those for the methylbarbaralones[4] where similar influences are evidently at work. The effects resulting from 1-substitution of the semibullvalenyl nucleus need not be comparable with those arising upon attachment of the same group at C-2. It is important to recognize specific bond weakening and strengthening effects on the *adjacent* and *remote* cyclopropane ring bonds as well as π-conjugative contributions which can arise in, *e.g.*, (**8b**) but not (**8a**). The effect of CH$_2^+$ (as in norcaradienylcarbinyl cations),[11] Me[8,12] and CN groups[13] on cyclopropane rings is to cause a lengthening of the adjoining ring bond and a shortening of the remote cyclopropyl C–C link. Geminal fluorine substitution has the opposite effect.[14]

Despite the variations in bond order, diverse substitution of the semibullvalene nucleus leads to unidirectional thermodynamic imbalance. It may well be that σ-derived substituent effects such as bond induction, hybridization, and electric-field contributions exert substantial impact.

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§ *E.g.*, ^{1}H n.m.r. data for (**7**): δ (CS$_2$; Me$_4$Si; $-57°$) 5·37 (dd, $J_{5,6}$ 2·0, $J_{6,7}$ 5·0 Hz, 6-H), 5·25 (dd, $J_{6,7}$ 5·0, $J_{7,8}$ 1·5 Hz, 7-H), 4·82 (m, 3-H), 3·03 (dd, $J_{1,5}$ 6·0, $J_{5,6}$ 2·0 Hz, 5-H), 2·84 (m, 1-H), 2·72 (m, 2- and 8-H), and 1·82 (d, J 1·5 Hz, Me).

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