APPRAISAL OF MIGRATORY APTITUDES IN THE $Mo(CO)_6$-PROMOTED BOND

RELOCATION OF [4.4.2]PROPELLA-2,4,11-TRIENES

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Thermal activation of [4.4.2]propella-2,4,11-triene and related molecules proceeds by

intramolecular $(4 + 2)\pi$ cycloaddition with formation of transient $\underline{cis}^2$-bishomobenzenes and

ultimately cyclooctatetraenes of isomeric structure.[1]   Incursion of a second symmetry-allowed

process, the [1,5]sigmatropic carbon shift, is not seen under such conditions. However, the

kinetically preferred Diels-Alder reaction can be blockaded and redirected in the presence of

a transition metal catalyst such as $Mo(CO)_6$,[2] the coordinative powers of which do not permit

involvement of all six pπ electrons during rearrangement. Among numerous hypothetical mecha-

nistic possibilities for the catalyzed process, we have considered [1,5]sigmatropic shifting

of a trigonal cyclobutene carbon (path a) or of a proximal methylene center (path b) to be

most plausible. Scheme I illustrates these alternatives without specifying either the rela-

tive stereochemistry of the complexing metal or the possibility that transient Mo-C bond

formation may be involved, but assuming η^4 coordination[2] for simplicity. These more refined

Scheme I

●denotes
deuterium
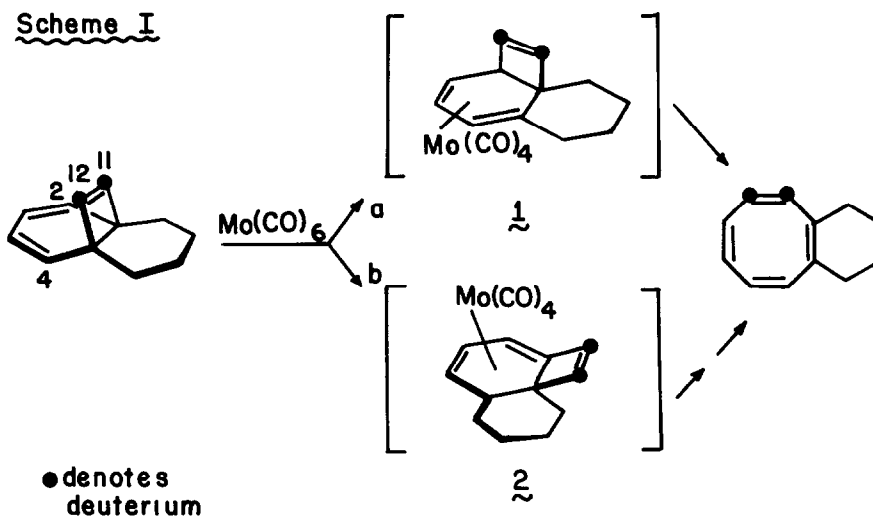
questions remain the subject of continued study. We see that path a is quite direct,
requiring valence isomerization and decomplexation of $\underline{1}$ (not necessarily in that order) to
provide the cyclooctatetraene derivative. Reaction coordinate b requires additional 1,5
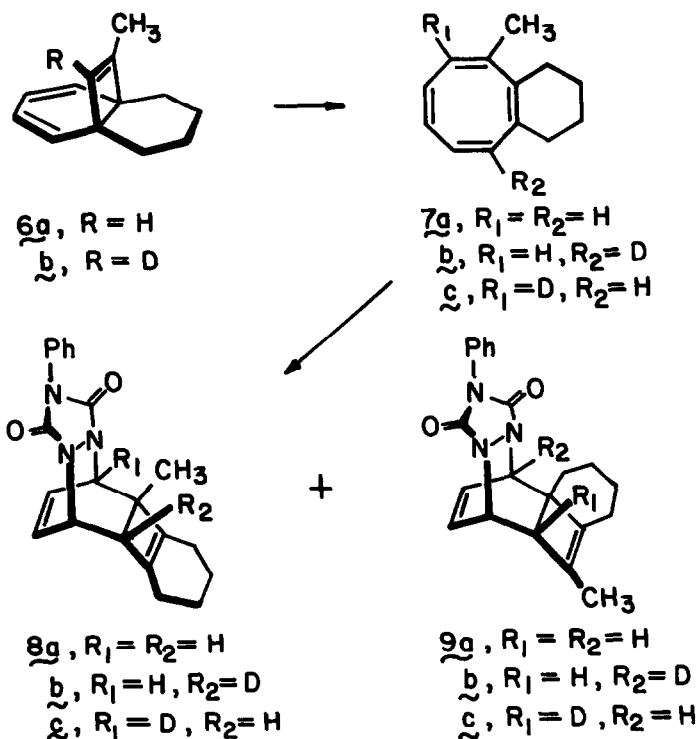hydrogen migration in $\underline{2}$ prior to delivering product.

In principle, a distinction between these pathways is realizable by suitable deuterium
labeling and by substitution at C_{11}. In the latter event, path a would be expected to dis-
play marked migratory selectivity since direct involvement of at least one cyclobutenyl car-
bon is required. Mechanism b should, on the other hand, not show a large C_{11}/C_{12} substituent
effect. In anticipation that the reaction terminus (C_2 or C_4) would also be predisposed
toward migratory bias, we have addressed this question as well.

The necessary compounds were accessible by earlier procedures.[3,4] Thus, $\underline{3}$ was prepared
by structural modification of the cyclohexene 1,2-dicarboxylic anhydride-butadiene-1,1,4,4-$\underline{d}_4$
adduct.[3] When heated at reflux with 0.5 mol equiv of $Mo(CO)_6$ in anhydrous benzene under N_2
for 36 hr, isomerization to $\underline{4}$ was observed. Structural assignment to this cyclooctatetraene
follows from its conversion with TCNE to adduct $\underline{5}$ of established isotopic substitution.[5]
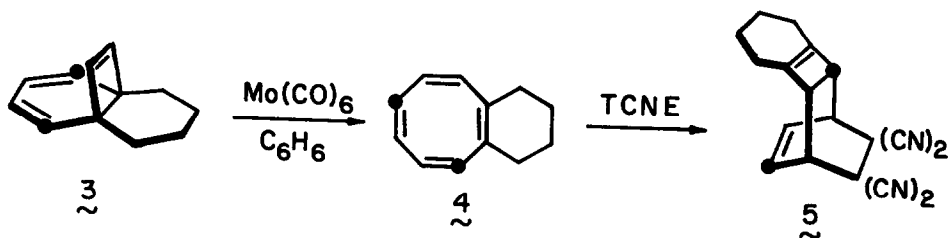
Treatment of $\underline{6a}$ with $Mo(CO)_6$ in analogous fashion resulted in the formation of $\underline{7a}$ (50%
vpc isolated). The spectral features of this hydrocarbon [pmr (CCl_4) δ 5.58-5.79 (m, 4),
5.24-5.46 (m, 1) and 1.5-2.1 (br m with spike at 1.80, 11)], its isolation as the exclusive
pyrolysis product of $\underline{6a}$, and its reaction with N-phenyltriazolinedione to give adducts $\underline{8a}$ (mp
164-165°)[6] and $\underline{9a}$ (mp 214-214.5°)[7,8] argue convincingly for 3-methyl substitution. Although
these point to an overwhelming preference for C_{12} migration, they do not distinguish between
the thermal and catalyzed processes. This issue was resolved with $\underline{6b}$, the pyrolysis of which
at 480° (vapor phase) led expectedly to $\underline{7b}$ as revealed by ultimate conversion to $\underline{8b}$[6] and $\underline{9b}$.[7]
In contrast, exposure of $\underline{6b}$ to $Mo(CO)_6$ as above gave $\underline{7c}$, the differing positioning of deu-
terium in which was clearly seen in $\underline{8c}$[6] and $\underline{9c}$.[7]

Although 2-methyl[4.4.2]propella-2,4,11-triene ($\underline{10}$) reacted with $Mo(CO)_6$ in refluxing

6a, R = H
b, R = D

7a, $R_1 = R_2 = H$
b, $R_1 = H, R_2 = D$
c, $R_1 = D, R_2 = H$

+

8a, $R_1 = R_2 = H$
b, $R_1 = H, R_2 = D$
c, $R_1 = D, R_2 = H$

9a, $R_1 = R_2 = H$
b, $R_1 = H, R_2 = D$
c, $R_1 = D, R_2 = H$

benzene with formation of an oily complex, heating of this latter substance in a Carius tube at 125° for 45 min (C_6H_6 solution) gave 12 in 87% yield. Direct metal-promoted isomerization could be effected directly (albeit less efficiently) in toluene solution. Pyrolysis of 10 was not as clean as usual. In addition to the major product characterized as 11, there was formed an exomethylene hydrocarbon tentatively formulated as the triene resulting from 1,5-H migration in 10. A distinction between 11 and 12 follows chiefly from mechanistic consideration of the pyrolysis results.[1a] The ready thermal isomerization of 13 exclusively to 12 provides additional circumstantial evidence. Moreover, the cyclooctatetraenes 7a, 11 and 12 exhibit patterns in the vinyl region of their pmr spectra which, although expectedly overlapping in chemical shift, are characteristic of the particular isomer. Using these spectral criteria, 13 has been found to rearrange in the presence of $Mo(CO)_6$ and benzene (80°) with formation of a mixture of 11 and 12, the 4-methyl derivative predominating slightly to the extent of 60-70%.

The present results are consistent with involvement of path a as the preferred reaction channel. The simplest mechanistic interpretation involves 1,5 sigmatropic displacement of one trigonal cyclobutene carbon while the other functions as a fulcrum. In 6, the rearrangement is highly regiospecific with the less substituted carbon shifting preferentially. Using 10 as
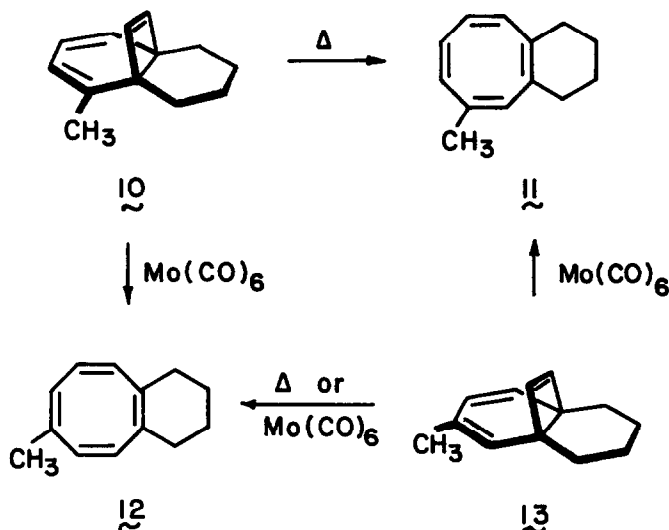
a model, we see a marked proclivity for migration toward the more highly substituted terminal

butadiene carbon.

The mechanistic test is still incomplete. In particular, the ultimate question of

whether these transformations represent the first authentic example of concerted sigmatropic

shifts in the coordination sphere of a transition metal remains to be convincingly established.

Notwithstanding, the strikingly specific nature of these rearrangements foreshadows a pro-

mising future for synthetic applications of transition metal catalysis.[9]

FOOTNOTES AND REFERENCES

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(6) Pmr (CDCl$_3$) δ 7.42 (m, 5), 6.19 (m, 2), 5.00 (m, 1), 4.63 (dd, J = 5 and 2 Hz, 1), 2.80
(br m, 1), 1.68 (br m, 8), and 1.45 (s, 3). In 8b, the signal at 2.80 is lacking, while
in 8c the 4.63 absorption is absent.

(7) Pmr (CDCl$_3$) δ 7.42 (m, 5), 6.20 (m, 2), 5.00 (m, 1), 4.71 (dd, J = 5 and 2.1 Hz, 1), 2.63
(br d, 1), 1.53 (s, 3), 1.50-1.92 (m, 1), and 1.10-1.50 (br m, 7). Adducts 9b and 9c
lack the 4.71 and 2.63 signals, respectively.

(8) Comparison of these data with that of the dimethyl congeners of unequivocally (X-ray)
established structure serves as additional confirmatory proof: L.A. Paquette, J.M. Photis,
K.B. Gifkins, and J. Clardy, to be published.

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