Applications of these new dienes in the arena of alkaloid total synthesis are under current investigation in these laboratories.

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Registry No. 1a, 65899-49-2; **1b**, 65899-50-5; (*E*,*E*)-**2a**, 86784-93-2; (*E*,*Z*)-**2a**, 86784-94-3; (*E*,*E*)-**2b**, 86802-62-2; (*E*,*Z*)-**2b**, 86821-99-0; (*E*,*E*)-**3a**, 86784-95-4; (*E*,*E*)-**3b**, 86802-63-3; (*E*,*E*)-**4a**, 86802-64-4; (*E*,*E*)-**4b**, 86784-96-5; **5**, 86784-97-6; **6**, 86784-98-7; **7**, 86784-99-8; **8**, 86785-00-4; **9**, 36715-51-2; **10**, 86785-01-5; **11**, 86785-02-6; **12** (isomer 1), 86785-03-7; **12** (isomer 2), 86785-04-8; **13**, 86785-05-9; **14**, 86785-06-0; **15**, 86785-07-1; **16**, 86785-08-2; **17**, 86785-09-3; **18**, 86785-10-6; **19**, 86785-11-7; **20**, 86802-65-5; TMSOTF, 27607-77-8; phenylsulfenyl chloride, 931-59-9; *N*-phenylmaleimide, 941-69-5; phenyl vinyl ketone, 768-03-6; acrolein, 107-02-8; 1-(phenylsulfinyl)-1,3-butadiene, 36715-34-1.

Stereochemical Course of Thermal Cycloreversion of [3.2.1]Propellanes to 1,3-Dialkenylcyclohexanes

Michael A. Blaustein and Jerome A. Berson*

Department of Chemistry, Yale University
New Haven, Connecticut 06511

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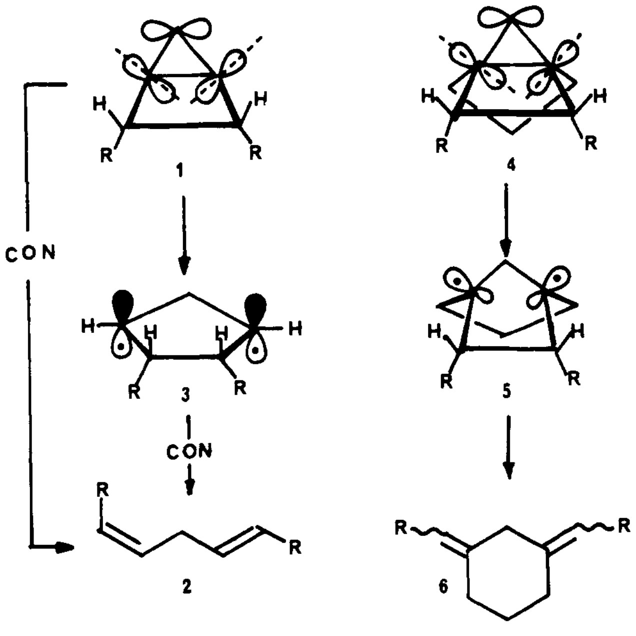
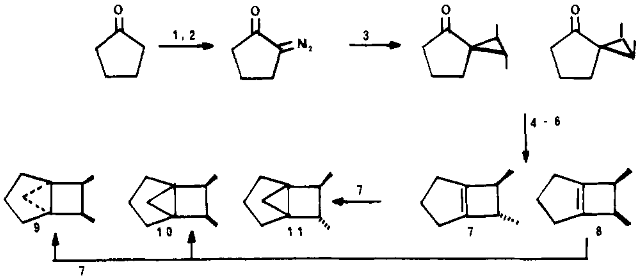
The observed conrotatory preference in the thermal cycloreversions of bicyclo[2.1.0]pentanes (**1**) to 1,4-pentadienes (**2**) has been discussed as an orbital symmetry effect operating in a concerted $[{}_2\sigma_s + {}_2\sigma_a]$ reaction[1] (Scheme I). The transition state is formed either directly from the bicyclic hydrocarbon or from the biradical **3**, in which the lower energy component of the frontier orbital linear combination is imagined to be C_s symmetric. In an effort to block access to the latter pathway, we now have studied the pyrolysis of the three 6,7-dimethyltricyclo[3.2.1.0^{1,5}]octanes ([3.2.1]propellanes), e.g., **4** ($R = CH_3$). Achievement of a planar local configuration at the bridgeheads in the corresponding biradical **5** would be opposed by severe geometric constraints. This work provides stereochemical supplementation of the important contribution of Aue and Reynolds,[2] who demonstrated the thermal cycloreversion in the unsubstituted [3.2.1]propellane (**4** → **6**, R = H).

Synthesis of the three stereoisomers of propellane **4** ($R = CH_3$) was accomplished as shown in Scheme II.[6] Cyclopropanation of trans olefin **7** gave the trans disubstituted propellane **11**, whereas the same procedure applied to cis olefin **8** gave a separable 4:1 mixture of cis disubstituted propellanes **9** and **10**, in which the CH_3 groups are, respectively, anti and syn to the cyclopropane CH_2 group. The anti vs. syn assignments are based upon the assumption that cyclopropanation occurs preferentially on the less hindered face of the double bond of **8** and the NMR chemical shifts of the methyl protons (δ 0.88 for **9** vs. 0.78 for **10**) and the 6- and 7-protons (δ 1.95 for **9** vs. 2.21 for **10**), which show the expected shielding effect of the cyclopropane ring.

Scheme I

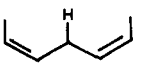


Scheme II[a]

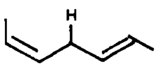


[a] Methods: (1) $Me_2NCH(OMe)_2$, 95 °C; (2) TsN_3, CH_2Cl_2, 25 °C, 24 h; (3) Ph_2CO, *cis*- or *trans*-2-butene, −30 °C, *hν* (>280 nm)[3]; (4) separation; (5) $TsNHNH_2$; (6) NaOMe, DME, <0.5 torr 165 °C;[4] (7) CH_2N_2, CuCl.[5]

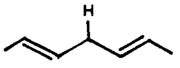
Stereochemical assignments to the three observed pyrolysis products **12**–**14** are based on the absence of symmetry in the ^1H and ^{13}C NMR spectra of **13** and on the following three criteria:



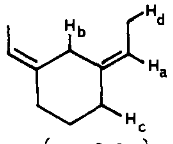
(2.76)



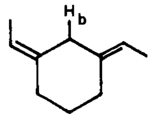
(2.67)



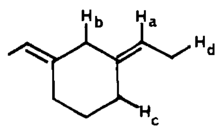
(2.61)



12 (H_b 2.88)



13 (H_b 2.82)



14 (H_b 2.76)

(1) chemical shifts (δ) of the doubly allylic methylene protons, which by analogy to those of the 2,5-heptadienes,[7] would be expected to resonate furthest downfield in the cis,cis isomer **12**, furthest upfield in the trans,trans isomer **14**, and at an intermediate position in the cis,trans isomer **13**, because of the deshielding effect of a nearby methyl group; (2) magnitudes of the observed homoallylic proton–proton couplings, which in model systems[8] are found to be larger in the transoid than in the cisoid configuration. (Double irradiation experiments at 500 MHz extracted the coupling constants $J_{cd} = 0.83$ and $J_{bd} < 0.35$ Hz for diene **12** and

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[1] Berson, J. A.; Bauer, W.; Campbell, M. M. *J. Am. Chem. Soc.* **1970**, *92*, 7515.

[2] (a) Aue, D. H.; Reynolds, R. N. *J. Org. Chem.* **1974**, *39*, 2315. (b) Reynolds, R. N. Ph.D. Thesis, University of California, Santa Barbara, CA, 1977, University Microfilms No. 78-587.

[3] Cf.: Jones, M.; Ando, W. *J. Am. Chem. Soc.* **1968**, *90*, 2200.

[4] Cf.: Kirmse, W.; Pook, K. H. *Angew.* Chem., *Int. Ed. Engl.* **1966**, *5*, 594.

[5] Cf.: Wiberg, K. B.; Burgmaier, G. J. *Tetrahedron Lett.* **1969**, 317.

[6] New substances were characterized by elemental composition and spectroscopic properties.

[7] Berson, J. A.; Olin, S. S. *J. Am. Chem. Soc.* **1969**, *91*, 777.

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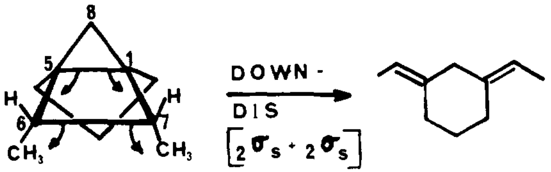
$J_{cd} < 0.35$ and $J_{bd} = 0.68$ Hz for diene **14**, which confirm the assignments based on criterion 1.); (3) nuclear Overhauser effects (proton–proton), maximized by spectral subtraction, which were detected for two pairs (H_d/H_a and H_d/H_b) in **12** (about 5% each, saturation of H_d) and for two pairs (H_a/H_b and H_a/H_d) in **14** (about 8% for H_b, saturation of H_a), in agreement with the above assignments.

Individual pyrolyses of propellanes **9**–**11** were carried out by flash vacuum (5×10^{-6} torr) pyrolysis (FVP) at temperatures between 520 and 690 °C and by static pyrolysis (sealed tubes, 100–200 torr) at 321 °C. At 520 °C, the total material balance was 97–99%. The percent yields of **12**, **13**, and **14**, respectively, were from **9**, 0.1, 0.5, and 99.4%, from **10**, 39.6, 47.8, and 12.6%, and from **11**, 3.6, 41.4, and 55.0%. Control experiments showed that the product compositions were not affected by interconversions among the stereoisomeric reactants or products and that the rates of pyrolysis of **9**–**11** did not differ significantly.

Our present interpretation of the data assumes that in the absence of strongly countervailing steric factors, the favored cycloreversion of [3.2.1]propellanes follows the "down-disrotatory" pathway exemplified by the highly stereospecific transformation **9** → **14**. This mode benefits from the same kind of steric preference that causes 3-methylcyclobutene to give *trans*-1,3-pentadiene,[10] but it also causes a steric clash of the exo substituents at C_6 and C_7 of the propellane with the syn hydrogen at C_8 in the transition state. Apparently, when one or both of the exo C_6 and C_7 groups are CH_3, as in **10** and **11**, the energy cost is sufficient to divert the cycloreversion into other pathways.



9 **14**

The underlying basis for the "down-disrotatory" preference is not obvious. As a [$_2\sigma_s + {}_2\sigma_s$] process, this mode is formally forbidden to be concerted by orbital symmetry. Moreover, the alternative mechanism via biradical **5** receives no support from presently available theory.[9] Extended Hückel calculations suggest that stretching of the bridge bond (C_1–C_5) of [3.2.1.]propellane leads neither to a total molecular energy minimum at the biradical geometry nor to a crossing of the antisymmetric and symmetric frontier energy levels. Such a crossing would be needed to produce the A-below-S ordering conducive to symmetry-allowed disrotatory cleavage of **5**.

A speculative interpretation of the "down–disrotatory" pathway as an orbital symmetry forbidden reaction facilitated by efficient overlap of the C_1–C_5 and C_6–C_7 orbitals in the transition state merits consideration.[11]

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Synthesis and Structure of $[PPN]_2[(\mu_2\text{-}CO)_3(CO)_9Cr_3(\mu_4\text{-}S)Cr(CO)_5]$: A Chromium Cluster[1]

M. Hoefler,* K.-F. Tebbe, H. Veit, and N. E. Weiler

Institut fuer Anorganische Chemie, Universitaet Koeln
D-5000 Koeln 41, Germany

Received March 25, 1983

Up to now, no fully characterized homogeneous chromium cluster has been known. There is only one compound reported in literature that should belong to this type of complexes, the $Na_2[Cr_3(CO)_{14}]$,[2] with either a linear or cyclic array of three chromium atoms, but no spectroscopic or structural details have been published so far. We were able to synthesize and characterize such a complex. Starting from the $[Cr_2(CO)_{10}SH]^-$ anion,[3] we enhanced the nucleophilicity of the complex by deprotonating[4] it to the deep green $[Cr_2(CO)_{10}S]^{2-}$ **1**. Treatment of **1** with excess $(CO)_5CrTHF$ (molar ratio = 1:2.2) leads to a change in color from green to red. After addition of [PPN]Cl[5] and recrystallization from acetone/ether, dark red crystals of **2**[6] can be obtained.

$$[PPN][\{(CO)_5Cr\}_2SH] \xrightarrow[THF]{NaH} Na[PPN][\{(CO)_5Cr\}_2S] \xrightarrow[2.\ [PPN]Cl]{1.\ (CO)_5CrTHF} \underset{\mathbf{2}}{[PPN]_2[(\mu_2\text{-}CO)_3(CO)_9Cr_3(\mu_4\text{-}S)Cr(CO)_5]}$$

In the solid state, **2** can be kept in air for some days without apparent decomposition.

An X-ray crystal-structure determination of **2**[7] revealed discrete cations and anions. The PPN cation shows no abnormities.[8] The anion (Figure 1) consists of a chromium triangle capped with a $SCr(CO)_5$ group. The basal chromium atoms are connected by single bonds, but there is no binding interaction with the other metal atom. All four S–Cr distances are in the range of single bonds; S–Cr4 is the longest of them. There are three terminal and two bridging CO ligands attached to each of the three basal chromium atoms, totaling to nine terminal and three bridging carbon monoxide ligands for the cluster part of the anion. If the metal–metal bonds are neglected, each of these three chromium atoms has a roughly octahedral surrounding with bond angles ranging from 163.5 (6)° to 175.4 (4)° (Table I) for opposite ligands. Cr4 carriers 5 terminal CO groups and is octahedrally coordinated. The whole $(CO)_5Cr$ group is somewhat bent toward Cr3. All carbon monoxide bridges are asymmetric, two of them to an extent as to classify them as semibridging.[9] Therefore, the bond lengths of the carbon monoxide bridges to one of the chromium atoms (Cr1) are quite different with 192.3 (12) pm

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(5) Solution in C_2H_5OH; molar ratio $[PPN]_2[\{(CO)_5Cr\}_2S]/[PPN]Cl$ = 1/1; $[PPN]^+$ = bis(triphenylphosphane)nitrogenium. *Chemical Abstracts* recommended name for $[PPN]^+$ is: bis(triphenylphosphoranediyl)nitrogen(1+).

(6) 37% yield, mp 163 °C, correct C, H, N, Cr elemental analysis, purification leads to composition $[PPN]_2[(CO)_{17}Cr_4S]\cdot(H_3C)_2CO$. The acetone can be removed by application of vacuum.

(7) The dark red crystals crystallize in the triclinic space group $P\bar{1}$, with unit cell constants a = 1477.2 (5), b = 1703.1 (3), c = 1950.0 (4) pm, α = 86.94 (2)°, β = 72.08 (2)°, γ = 70.84 (2)°. The structure was refined to values $R_F = 0.083$ and $R_W = 0.100$. 5902 independent reflections with $|F| \geq 3\sigma(F)$ were used.

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