analysis (paper in preparation), for which we are indebted to Professor Richard Adams and Ms. Nancy Golembeski.

(7) (a) The stereochemical assignment of the major isomer as 9 and the minor one as **10** is arbitrary and could be reversed without effect on the present study. The configurations are assigned here by NMR chemical shift differences analogous to those observed in the 2-methoxybicyclo[2.1.0]pentanes.[7b,c] (b) E. L. Allred and R. L. Smith, *J. Am. Chem. Soc.*, **89**, 7133 (1967); (c) *ibid.*, **91**, 6766 (1969).

(8) This analysis of the partition of the photochemical intermediate is based on the unproven assumption that loss of N_2 gives a singlet TMM with intact deuterium stereochemistry as the first product. Other mechanisms compatible with the data may be imagined.

(9) Although we consider the data for toluene-d_8 solution to be more reliable, the rate constant in $CDCl_3$-$CFCl_3$-Eu(fod)$_3$ is approximately the same.

(10) (a) D. M. Hood, H. F. Schaefer, III, and R. M. Pitzer, *J. Am. Chem. Soc.*, **100**, 8009 (1978). Cf., however, (b) M. P. Conrad, R. M. Pitzer, and H. F. Schaefer, III, *ibid.*, **101**, 2245 (1979); (c) M. S. Platz and J. A. Berson, *ibid.*, **99**, 5178 (1977); (d) P. Dowd and M. Chow, *ibid.*, **99**, 6438 (1977).

(11) The evidence that TMM **11** has a triplet ground state consists of the observations of a long-lived triplet signal, when 7a is irradiated in a glassy matrix at 77 K,[12] and a typical dilution effect[13] in cycloaddition reactions of the TMM with olefins.

(12) We thank Mr. E. F. Hilinski for this experiment.

(13) Compare (a) J. A. Berson, L. R. Corwin, and J. H. Davis, Jr., *J. Am. Chem. Soc.*, **96**, 6177 (1974); (b) J. A. Berson, C. D. Duncan, and L. R. Corwin, *ibid.*, **96**, 6175 (1974).

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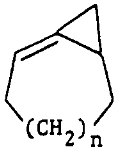
Mechanisms of Dimerization and Rearrangement of a Bicyclo[3.1.0]hex-1-ene

Sir:

Bicyclo[3.1.0]hex-1-ene (**1a**) and 5-methylenebicyclo[2.1.0]pentane (**2a**) are hypothetically related through a common trimethylenemethane (TMM) biradical **3**. Members of the **2a** series seem to be so precariously balanced on the edge of covalency that their bridge bond (C*-C*) may have a negative dissociation energy (DE); that is, the (triplet) ground state of the biradical may be more stable than the bicyclic hydrocarbon.[1,2]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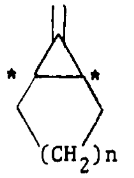
b: n = 1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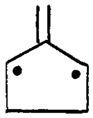
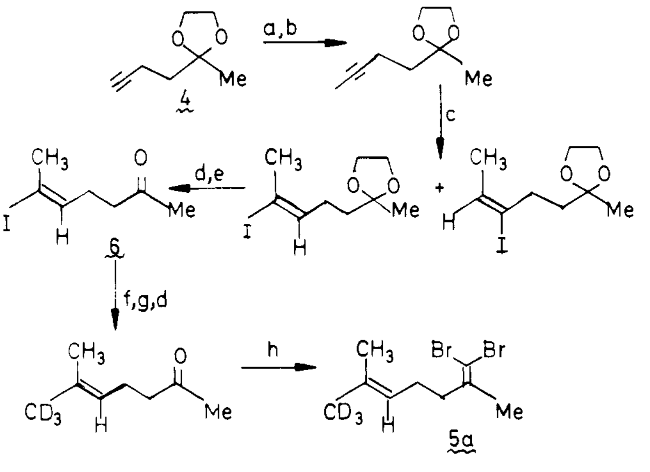
b: n = 1


3

By analogy to the next higher homologous pair, **1b** and **2b**, in which the isomer (**1b**) with the endocyclic double bond is of much higher energy,[3] one might predict the energy ordering **1a** > **2a**. With reference to the TMM **3**, **1a** therefore might be even more likely than **2a** to embody a bond with a negative DE. In this paper, we report some reactions of a putative member of the **1a** series which tend to confirm the **1a** > **2a** order of energies.

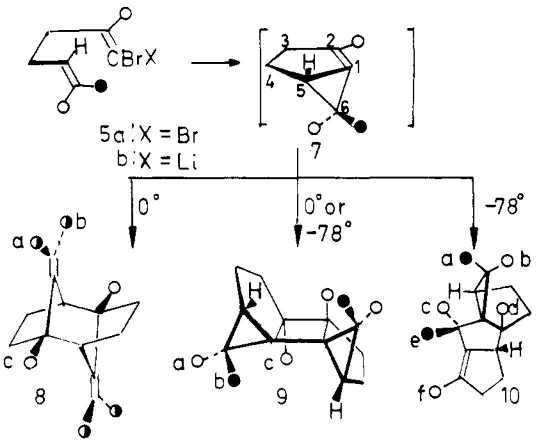
Scheme I outlines the synthesis of 1,1-dibromo-2-methyl-6-*trans*-trideuteriomethylhepta-1,5-diene (**5a**) from the known[4a] acetylenic ketal **4**. The key step is the hydrozirconation[4b]-iodination sequence leading to compound **6**. Although not highly regiospecific, this step gives **6** and ultimately **5a** with complete (>95%) stereospecificity, as judged by integration of the NMR signals of the geminal allylic methyl groups. Undeuterated **5a** (CH_3 instead of CD_3) shows resonances at δ 1.68 and 1.61. The δ 1.68 absorption disappears completely in **5a**.

Scheme I[a]



[a] Methods: (a) $LiNH_2/NH_3$ (l)/THF, −78 °C; (b) MeI, 0 °C, THF; (c) $Cp_2Zr(H)Cl$, PhH, 4 h, then I_2, following a general procedure of ref 4b; (d) H_3O^+; (e) separation by GC; (f) $HOCH_2CH_2OH$, TsOH, PhH; (g) CD_3Li, 5% CuBr, following a general procedure of ref 4c; (h) CBr_4, Ph_3P, $PhCH_3$, 12 h, 110 °C, following a general procedure of ref 5, modified.

Scheme II



As has been previously reported in the unlabeled series,[6,7] α-elimination from 1-halo-1-lithio-2,6-dimethylhepta-1,5-dienes leads to two major types of products derived from a trimethylbicyclo[3.1.0]hex-1-ene (**7**, Scheme II, ● = ○ = ◑ = CH_3): (i) a mixture of dimers of the trimethylenemethane (TMM) **11**, among which is the crystalline, highly symmetrical compound **8**, and (ii) the symmetrical [2 + 2] dimer **9**. The latter product predominates at low temperature. We now find that the reaction mixture generated from **5a** and MeLi in Et_2O at −78 °C also contains ~5% a third dimer which can be isolated by gas chromatography (GC) on a 15% OV-17 column. This compound, assigned structure **10** by its spectroscopic properties,[8] is clearly related to the analogue **10** (H instead of Me groups a, b, c, e) obtained[7] from 1,1-dibromo-2-methylhexa-1,5-diene under similar conditions.

Metalation of stereospecifically deuterated **5a** (Scheme II, ● = CD_3, ○ = CH_3, ◑ = $CD_3/2$) gives via **5b** stereospecifically deuterated **9** and **10**. At normal isotopic abundance, **9** shows three different six-proton methyl-group NMR resonances (Bruker HX-270) at δ 1.16, 1.03, and 0.99, but **9**-d_6 generated from **5b**-d_3 shows two six-proton singlet absorptions at δ 1.16 and 1.03 but no absorption at δ 0.99. This suggests that carbenoid cyclization of **5b** onto the isopropylidene group is stereospecific (presumably cis), and that the intermediate

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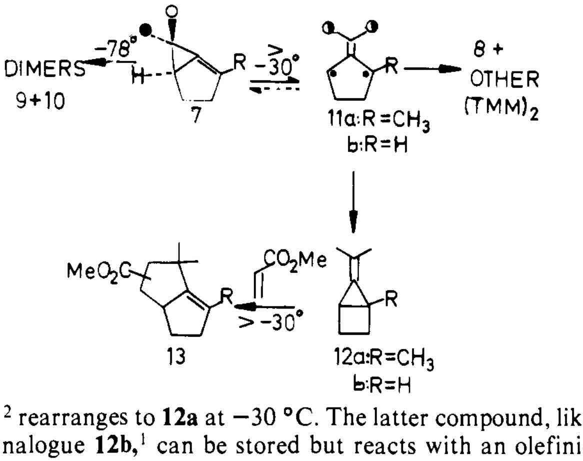
dimerizes without perturbation of the configuration at C_6. When unlabeled, compound **10** shows six three-proton singlets corresponding to methyl groups a-f. Two of the signals of **10**-d_6, examined in benzene-d_6, completely disappear leaving four undiminished CH_3 resonances. This finding, taken together with the observations on **8** (below), supports the previous conclusion[7] that products of the $[\sigma + \pi]$ cycloaddition mode do not involve a TMM intermediate.

However, compound **8** is formed with exactly 1.5 deuterium atoms in each of the allylic methyl groups a and b, as can be deduced from the signals at δ 1.79 and 1.69, each of which is just half as intense as the 6-proton singlet of the c Me groups at δ 1.22. Note that the [2 + 2] dimer **9** formed in the same reaction mixture at 0 °C still shows completely stereospecific labeling, as at −78 °C.

These observations may be explained by a mechanism in which **8** is formed from the TMM **11a** by the sequence **7** → **11a** → **8**. The TMM **11a** lives long enough as the singlet biradical to undergo complete stereorandomization by torsion about the exocyclic C-C bond,[2,9] but ring closure back to the bicyclo[3.1.0]hex-1-ene **7** is slow on the time scale of dimerization.

Ring closure of a TMM of type **3** to structure **1a** thus seems to be unfavorable, as is also suggested by the highly specific formation of 5-alkylidenebicyclo[2.1.0]pentanes (**2a**) in the photolysis of 7-alkylidene-2,3-diazanorbornenes,[1,2,10] presumably via a TMM intermediate. Another instance of this now appears in the apparently unidirectional thermal rearrangement of the bicyclo[3.1.0]hex-1-ene **7** to the 5-alkylidenebicyclo[2.1.0]pentane **12**. Metalation of **5a** (undeuterated) at −30 °C, cooling, and treatment with MeOH at −78 °C, storage for 8 min, addition of methyl acrylate, and warming to room temperature give not only dimers **9, 10,** and **8,** but also ~20% of a mixture of 1:1 cycloadducts of the familiar[11] type **13.** Apparently, **7,** which only dimerizes at −78 °C,[12] rearranges to **12a** at −30 °C. The latter compound, like its analogue **12b,**[1] can be stored but reacts with an olefinic trapping agent at higher temperature.[13]



The present results suggest that the transition state leading from **11a** to **7** must be substantially higher in energy than that leading to **12a.** It seems likely that this energy ordering may apply to the bicyclic molecules themselves. Hence, bicyclo[3.1.0]hex-1-enes (**1a**), like 5-alkylidenebicyclo[2.1.0]pentanes (**2a**), may contain a bond whose rupture to give the ground-state triplet TMM common to both bicyclic species is nearly thermoneutral if not actually exothermic.

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(2) M. G. Lazzara, J. J. Harrison, M. Rule, and J. A. Berson, *J. Am. Chem. Soc.*, preceding paper in this issue.

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(4) (a) J. B. Heather, R. Sood, P. Price, G. P. Peruzzotti, S. S. Lee, L. H. Lee, and C. J. Sih, *Tetrahedron Lett.*, 2313 (1973); (b) D. W. Hart, T. F. Blackburn, and J. Schwartz, *J. Am. Chem. Soc.*, **97**, 679 (1975). (c) J. F. Normant, J. Villieras, G. Cahiez, and A. Commercon, *C. R. Acad. Sci., Ser. C*, **278**, 967 (1974).

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(6) (a) G. Köbrich and H. Heinemann, *Chem. Commun.*, 493 (1969); (b) G. Köbrich, *Angew. Chem., Int. Ed. Engl.*, **12**, 464 (1973).

(7) M. Rule and J. A. Berson, *Tetrahedron Lett.*, 3191 (1978).

(8) Compound **10** shows NMR singlets at δ 1.69, 1.21, 1.19, 1.00, 0.78, and 0.71 (3 H each, CH_3) and a multiplet at δ 2.66–2.45 (3 H, allylic H). The mass spectrum shows a parent peak at *m/e* 244, corresponding to $C_{18}H_{28}$.

(9) Stereorandomization cannot be distinguished by this experiment from a stereospecific reaction involving an even number of olefinic torsions of the exocyclic double bond in one partner and an odd number in the other. We consider this an unlikely alternative.

(10) M. G. Lazzara, Ph.D. Dissertation, Yale University, planned for 1979, finds traces (1–3%) of adducts of **1a** type products in some instances.

(11) Cf. J. A. Berson, *Acc. Chem. Res.*, **11**, 446 (1978), and references cited there.

(12) In a control experiment, we find that metalation of **5a** at −78 °C instead of −30 °C, followed by the same treatment, gives no cycloadducts **13** but only the usual dimers **9** and **10** obtained in the absence of methyl acrylate.

(13) It is still not clear whether the cycloadditions of **12a** and **12b** with olefins occur directly or by preliminary formation of singlet diyls **11a** and **11b.**

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Synthesis and X-ray Characterization of the $[M_6N(\mu\text{-}CO)_9(CO)_6]^-$ (M = Co, Rh) Anions. A New Class of Metal Carbonyl Cluster Compounds Containing an Interstitial Nitrogen Atom

Sir:

We report here the first examples of carbonyl cluster compounds containing interstitial nitrogen: the $[M_6N(CO)_{15}]^-$ (M = Co, Rh) anions.

The reaction of $K_2[Co_6(CO)_{15}]$[1] in THF with $NOBF_4$[2] gives a mixture of Co(II), $Co(CO)_3NO$, traces of $Co_4(CO)_{12}$, and the new anion $[Co_6N(CO)_{15}]^-$ which is separated as the orange-red potassium salt (40–50% yield) by evaporation to dryness, dissolution in MeOH, and filtration from KBF_4, followed by precipitation with water and concentration in vacuo.

The similar reaction of $[Rh_6(CO)_{15}]^{2-}$ [3] with $NOBF_4$ gives only very low yields of the analogous rhodium compound (<10%).[4] However, better yields (40–60%) of $K[Rh_6N(CO)_{15}]$ have been obtained from the reaction of a methanolic solution of $K_3[Rh_7(CO)_{16}]$[3] with a 1:1 mixture of CO and NO followed by filtration, precipitation of the yellow potassium salt by addition of aqueous KCl (3%), concentration in vacuo, filtration, and washing the precipitate with water until the washings are colorless.

The potassium salts can be transformed into the $[(Ph_3P)_2N]^+$ (PPN^+) or Ph_4P^+ salts by metathesis in aqueous Pr^iOH.

The structure of $PPN[Co_6N(CO)_{15}]$[5] has been investigated

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