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[1.1.1]PROPELLANE: REACTION WITH FREE RADICALS

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Summary [1.1.1]Propellane is more reactive towards free radicals than bicyclo[1.1.0]butane, and much more reactive than bicyclo[2.1.0]pentane. Therefore, the reactivity is not determined by strain energy relief or the HOMO energy. The addition of acetaldehyde is unique in that a 1:2 adduct is formed. A number of other additions are described, and provide convenient routes to 1,3-disubstituted bicyclo[1.1.1]pentanes.

A study of the relative reactivity of bicyclo[1.1.0]butane (**1**), bicyclo[2.1.0]pentane (**2**) and [1.1.1]propellane (**3**) provides a unique opportunity to examine the factors which determine reactivity. If the transition state for a process involving an electron deficient species (i.e., a carbocation, a free radical or an electron deficient alkene) lies early along the reaction coordinate, one might expect the HOMO energy, or the ionization potential, to be a controlling factor.[1] On the other hand, if the transition state lies late along the reaction coordinate, the rate of reaction should respond to the overall energy change.[2] It is also possible that the rate would correlate with the local concentration of charge near the bridgehead carbon as measured by $-\nabla^2\rho$.[3] These quantities are compared for **1**-**3** in Table I. It can be seen that **1** has the lowest ionization potential,[4] **2** gives the largest energy change, and **3** has the largest value of $-\nabla^2\rho$.


1


2

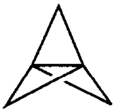
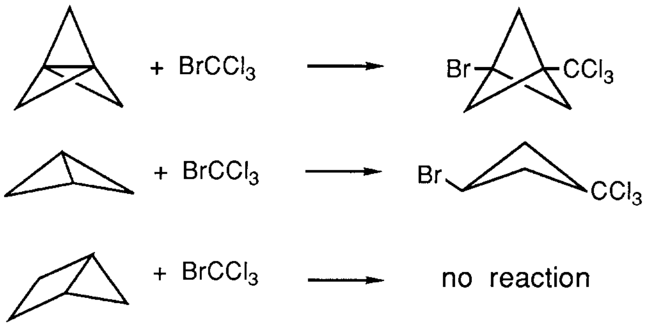

3

Table I

Properties of Cycloalkanes

Property	**1**	**2**	**3**
Ionization Potential (eV)	9.3	9.6	9.7
Strain Energy Relief (kcal/mol)	37	49	30
Local charge concn ($-\nabla^2\rho$)	0.19	0.23	0.33

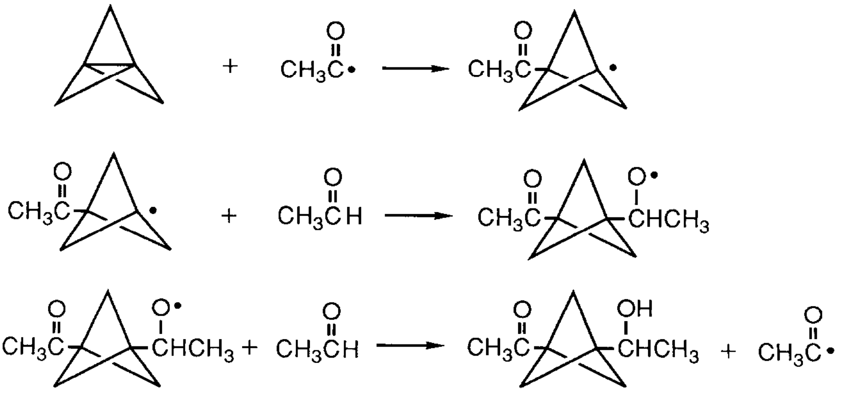
We are examining the reactivies of these compounds in a number of types of reactions, and now wish to report the results of a study of free radical chain processes involving addition to the central bonds. Both 1 and 3 react readily with bromotrichloromethane to give addition across the central bonds, but 2 did not react in 24 hr. These reactions almost certainly are free radical chain processes involving the tricloromethyl radical as the chain carrying species.[5]



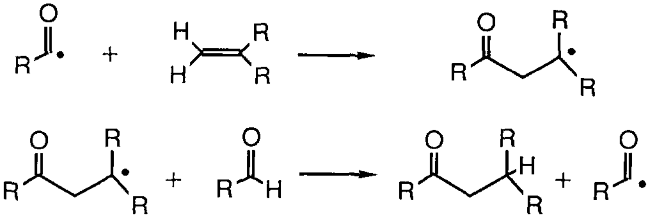
The low reactivity of 2, despite the large driving force for reaction shows that cleavage of the central bond has not proceeded very far at the transition state.

When a mixture of 1 and 3 was dissolved in carbon tetrachloride, a slow reaction occurred leading again to addition across the central bond. The reaction of 3 was more rapid than that of 1 by a factor of 5:1. The ionization potentials would have predicted the opposite reactivity order. Of the properties listed above, only the local charge concentration correlates with the observed reactivity.

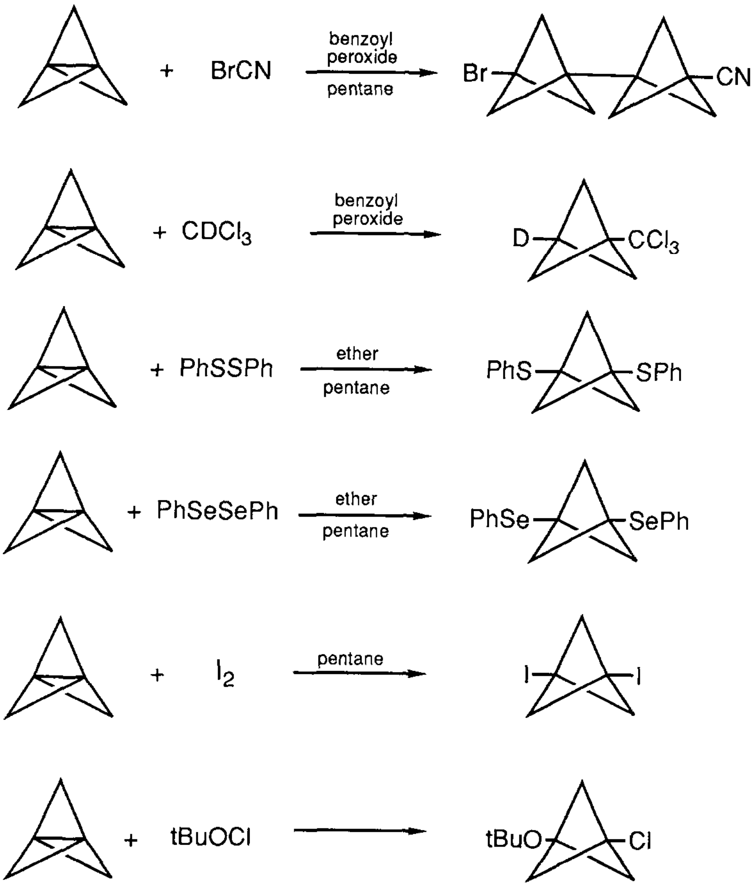
Many other free radical additions have been observed. The benzoyl peroxide catalyzed addition of acetaldehyde to 3 was particularly interesting in that it led to a 2:1 adduct. If the acetyl radical is accepted as the chain carrying species, the reaction would occur as follows:



This mode of addition is unusual. Free radical additions of aldehydes to alkenes normally give 1:1 adducts:[6]



Other examples of free radical additions include:



The reaction with cyanogen bromide gave very little 1:1 adduct. The 2:1 adduct shown is the major product, with a significant amount of the corresponding 3:1 adduct also being formed. A small amount of 2:1 adducts was observed in some other reactions, particularly in the addition of chloroform and carbon tetrachloride.

In view of the facile synthesis of **3** recently described by Semmler, Szeimies and Belzner,[7] these reactions represent the most effective means of preparing 1,3-disubstituted bicyclo[1.1.1]pentanes. The details of these and related reactions will be reported subsequently.

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References

1. Fleming, I. "Frontier Orbitals in Organic Chemistry," Wiley, NY, 1976, p. 24.
2. The strain energies of **1** - **3** and of the compounds formed by cleavage of the central bonds were derived from the ΔH_f given in Wiberg, K. B. *J. Am. Chem. Soc.* **1983**, *105*, 1227.
3. Bader, R. F. W.; MacDougall, P. J.; Lau, C. D. H. *J. Am. Chem. Soc.* **1984**, *106*, 1594. The details of the calculations will be presented at another time.
4. Honegger, E.; Huber, H.; Heilbronner, E.; Dailey, W. P.; Wiberg, K. B. *J. Am. Chem. Soc.* **1985**, *107*, 7172.
5. Huyser, E. S., "Free Radical Chain Reactions," Wiley, NY, 1970, pp. 148-151.
6. Huyser, E. S. *Ibid* pp. 151-154.
7. Semmler, K.; Szeimies, G.; Belzner, J. *J. Am. Chem. Soc.* **1985**, *107*, 6410.

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