

A:E ratio is lower than the calculated ratio, indicating contributions from the other two radical pairs. The relative contributions made to the polarization by the three radical pairs cannot, however, be determined by this method.

A study of the photochemistry of acetone⁷ indicates that the disproportionation of $[(\text{CH}_3)_2\dot{\text{C}}(\text{OH})(\text{OH})\dot{\text{C}}(\text{CH}_3)_2]^{\text{F}}$ to give the alcohol plus the enol of acetone $\text{CH}_2\text{C}(\text{OH})\text{CH}_3$ is responsible for at least part of the observed polarization of alcohol. It seems reasonable to expect that this path occurs in the present case, also. Unfortunately, the generation of $[(\text{CH}_3)_2\dot{\text{C}}(\text{OD})(\text{OD})\dot{\text{C}}(\text{CH}_3)_2]^{\text{F}}$ by using D_2O in place of H_2O is not a good test of this path since $[(\text{CH}_3)_2\dot{\text{C}}(\text{OD})\dot{\text{C}}\text{H}_2\text{CH}(\text{OD})\text{CH}_3]^{\text{F}}$ and $[\text{CH}_3\text{CH}(\text{OD})\dot{\text{C}}\text{H}_2\dot{\text{C}}\text{H}_2\text{CH}(\text{OD})\text{CH}_3]^{\text{F}}$ can contribute to the alcohol polarization, also. Thus although alcohol polarization is observed when D_2O is the solvent (Figure 1D), we can conclude only that enol formation may be occurring, and this may be *via* any or all of these radical pairs.

None of the above mentioned radical pairs can account for the negative polarization observed for acetone since they either give no net polarization or, in the case of $[(\text{CH}_3)_2\dot{\text{C}}(\text{OH})\dot{\text{C}}\text{H}_2\text{CH}(\text{OH})\text{CH}_3]^{\text{F}}$, net positive polarization for acetone. Consequently, we attribute the negative polarization to the formation of acetone *via* the radical pairs $[(\text{CH}_3)_2\dot{\text{C}}(\text{OH})\text{R}_1]^{\text{F}}$ and $[(\text{CH}_3)_2\dot{\text{C}}(\text{OH})\text{R}_2]^{\text{F}}$ whereas $[\text{CH}_3\text{CH}(\text{OH})\dot{\text{C}}\text{H}_2\text{R}_1]^{\text{F}}$ and $[\text{CH}_3\text{CH}(\text{OH})\dot{\text{C}}\text{H}_2\text{R}_2]^{\text{F}}$ give positive polarization. R_1 and R_2 indicate forms of $\dot{\text{O}}\text{H}$ or $\dot{\text{O}}_2\text{H}$ complexed with $\text{Ti}(\text{IV})$. For the last two radical pairs, acetone must result from a disproportionation to give the enol $\text{CH}_2\text{C}(\text{OH})\text{CH}_3$ which presumably under the aqueous acid conditions might convert to acetone at a rate which is competitive with the spin-lattice relaxation rates of the protons.

The fact that the nmr technique provides evidence for radical reactions not detected by esr⁴ (and *vice versa*) indicates the complementary fashion in which these techniques may be employed in studying reaction mechanisms of radicals generated by TiCl_3 plus H_2O_2 . The reactions proposed in this paper could perhaps account for the deviation from first order found for the decay rates of the organic radicals measured in the esr study.

Acknowledgments. This work has been supported in part by the National Research Council of Canada (M. C. and C. A. F.) and the donors of the Petroleum Research Fund, administered by the American Chemical Society (M. C.).

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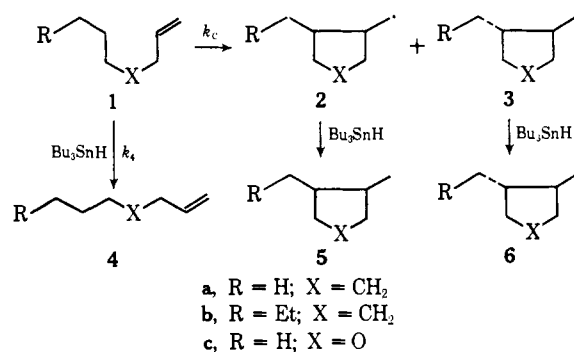
Preferential Cis Cyclization of 6-Hepten-2-yl and Related Radicals. An Example of Orbital Symmetry Control

Sir:

Previous work has afforded conflicting evidence concerning the stereochemical course of intramolecular

addition in suitably substituted alkenyl radicals. Although earlier studies¹ indicated that 6-hepten-2-yl radical, **1a**, gives predominately the cis isomer of the cyclic product, the most recent report² suggests that **1a** undergoes exclusive trans cyclization. We now present evidence that the cis mode of cyclization is favored in 6-hepten-2-yl radical, **1a**, and two related species,³ **1b** and **1c**, and we offer an explanation for this "perplexing"⁴ phenomenon.

Treatment of 6-chlorohept-1-ene with tributylstannane in pentane^{5,6} at 65° gave 1-heptene (**4a**), *cis*- and *trans*-1,2-dimethylcyclopentane (**5a** and **6a**), and a trace of



methylcyclohexane, each of which was unequivocally identified by comparison with authentic compounds.⁷ The relative yields of cyclized and straight-chain products, determined by gas chromatography,⁸ were related in the expected way to the initial concentration of stannane,^{2,6,9} but the *cis*:*trans* ratio remained constant within the limit of experimental error. Similar results were obtained when the radicals **1b** and **1c**, were generated from the appropriate chloro compounds by treatment with tributylstannane.

Steady-state treatment of the dependence of the yields of cyclized products from each radical on initial stannane concentration enabled *k_c*/*k₄* to be calculated,^{2,9} where *k_c* represents the rate constant for total cyclization. The rate constant for hydrogen atom transfer from stannane, *k₄*, is expected⁶ to have a value of $\sim 10^6 \text{ M}^{-1} \text{ sec}^{-1}$. The results (Table I) show that the two radicals, **1a** and **1b**, have similar values of *k_c*, but the oxygen-containing radical **1c** cyclizes much more rapidly. Replacement of a methylene group by an oxygen atom in an equivalent position in *o*-3-butenyl-phenyl radical has been shown previously to cause a similar rate enhancement.¹⁰

The data clearly show that for each of the radicals

- (1) N. O. Brace, *J. Org. Chem.*, **32**, 2711 (1967).
- (2) C. Walling and A. Cioffari, *J. Amer. Chem. Soc.*, **94**, 6059 (1972).
- (3) The bicyclic products formed from butenylcyclohexyl radical also arise mainly by a *cis* cyclization process. Details will be presented in a later paper.
- (4) J. W. Wilt in "Free Radicals," Vol. I, J. K. Kochi, Ed., Wiley, New York, N. Y., 1973, p 426.
- (5) H. G. Kuivila, *Accounts Chem. Res.*, **1**, 299 (1968).
- (6) D. J. Carlsson and K. U. Ingold, *J. Amer. Chem. Soc.*, **90**, 7047 (1968).
- (7) Starting materials and reference compounds were commercial materials or synthesized by unequivocal routes. They had spectroscopic and physical properties (nmr, ir, and mass spectra and refractive indices) consistent with the proposed structures. New compounds gave satisfactory microanalytical data.
- (8) Gas chromatography was carried out on an Apiezon L 100 m × 0.508 mm capillary column at 65° with nitrogen carrier gas (0.5 ml min⁻¹).
- (9) A. L. J. Beckwith and G. Phillipou, *J. Chem. Soc., Chem. Commun.*, 280 (1973).
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Table I. Stereochemistry and Relative Rate Constants for Cyclization of 6-Hepten-2-yl and Related Radicals at 65°^a

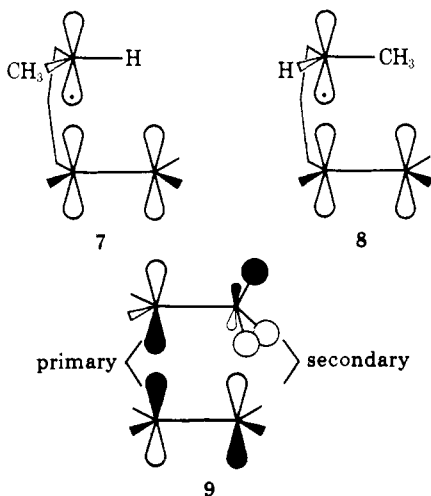
Radical	k_c/k_t^b	cis/trans
1a	0.26	2.3
1b	0.30	2.3
1c	3.0	2.3

^a Total yields of products were >80%; they were normalized to 100% for computational purposes. ^b Determined over a four-fold range of initial stannane concentration.

1a-c the cis mode of cyclization is favored. The observed cis:trans ratios are mutually consistent and in reasonable agreement with those obtained in some of the earlier work.¹ It thus appears that preferential cis cyclization may be a general feature³ of radicals containing the 6-hepten-2-yl system.¹¹

On simple thermodynamic grounds trans cyclization would be expected to be more favorable than cis, since the transition state, 7, for the former process is less subject to nonbonded repulsions than is that for the latter, 8.⁴ However, application of orbital symmetry considerations¹² affords a contrary view.

One model for the transition state for alkyl radical addition to an olefinic bond involves interaction of the half-filled p orbital with the vacant π^* orbital.¹³ Hyperconjugative mixing^{14,15} of the former with adjacent CH σ and σ^* orbitals produces a modified delocalized orbital¹⁶ which is of similar symmetry to the acceptor π^* orbital. Thus, in the transition state, 8, leading to cis disubstituted product there is a secondary attractive interaction between the alkyl substituent and the olefinic bond (see 9) which is not available in the transition state, 7, for trans cyclization.



Hoffmann, Levin, and Moss¹⁵ have pointed out that such interactions should be important only in highly exothermic reactions where the transition state occurs at large separation of the reaction partners. The re-

(11) However, preferential cis cyclization is not exhibited by 1-substituted hex-5-enyl radicals in which the free electron is delocalized onto substituents such as cyano, carboxy, or phenyl: M. Julia and M. Maumy, *Bull. Soc. Chim. Fr.*, 434 (1966); C. Walling and A. Ciofari, *J. Amer. Chem. Soc.*, **94**, 6064 (1972).

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actions described here, having ΔH of approximately -18 kcal/mol, appear to meet these criteria.

Finally, our results and those previously recorded strongly suggest that cyclopolymers formed from suitable 1,6-diolefins¹⁶ probably comprise predominantly cis disubstituted five-membered cyclic units.

Acknowledgment. This research was supported by the Australian Research Grants Committee. One of us (G. P.) gratefully acknowledges a Commonwealth Postgraduate Award.

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Structurally Isomeric and Diastereoisomeric Adducts from the Nitration of 1,2,4-Trimethylbenzene. The Orientation and Mechanism of Side-Chain Substitution of Arenes

Sir:

Several nitronium acetate (acetyl nitrate) *cis* and *trans* adducts which contain the 4-nitro-1,4-dihydrophenyl moiety have been isolated from nitration of methylbenzenes and substituted methylbenzenes in acetic anhydride.¹⁻⁴ We wish to report the first example of the formation of structurally isomeric adducts. Our results also show that 1,4 adducts are intermediates in side-chain substitution of arenes under electrophilic conditions^{5,6} and unambiguously reveal the orientation of such substitution.

Nitration of pseudocumene (1,2,4-trimethylbenzene) at -45° gave a mixture⁷ which contained 50% dienes. The acetoxy-nitro dienes 1a, 1b, 2a, and 2b were isolated by low-temperature chromatography. The general arguments for the assignment of the 1,4-adduct structure have been given elsewhere.^{3,8,9} Nmr shift reagent studies using Eu([²H₉]fod)₃ made possible the crucial assignment of the 1 and 2 structures. The reagent complexes preferentially at the acetate group,¹⁰ and thus the structure 1 was assigned to that pair of isomers in which, on the addition of the reagent, the methyl doublet moved less rapidly and the lone vinyl proton moved more rapidly downfield than in the other pair.

The reactions of 1 and 2 parallel those of the *p*-xylene adducts^{2,11} depicted in Scheme I. Both 1 and 2 under-

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