polarimetric run was prepared; α_{obsd} of this solution agreed within 7% with that observed for the end point of the kinetic run. Because of the strong absorbances in the ultraviolet region by the host's naphthalene rings and the *p*-nitrophenyl ester group, the rate of ethanolysis of the thiol ester intermediate could not be followed spectrophotometrically.

References and Notes

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Ground States of Molecules. 55.[1] MINDO/3 Study of Rearrangements of C_4H_7 Radicals

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Abstract: MINDO/3 calculations are reported for seven stationary points on the C_4H_7 potential surface, corresponding to various isomeric C_4H_7 radicals and the transition states for their interconversion. The results are consistent with the available experimental evidence.

Introduction

One of the first well-defined rearrangements of free radicals to be reported involved the isomerization of alkenyl radicals formed by addition of isopropyl or *tert*-butyl radical to acetylene in the gas phase.[3-6] Thus, isopropyl radical (**1**) was found to react with acetylene (**2**) to form 1-pentene (**3**) as well as the expected 3-methyl-1-butene (**4**) (eq 1).

$$\underset{\mathbf{1}}{(CH_3)_2CH} + \underset{\mathbf{2}}{HC{\equiv}CH} \longrightarrow \underset{\mathbf{3}}{CH_3CH_2CH_2CH{=}CH_2} + \underset{\mathbf{4}}{(CH_3)_2CH{-}CH{=}CH_2} \quad (1)$$

The first step in the reaction must involve formation of the vinyl radical **5**, which is converted to **4** by abstraction of hydrogen from some other molecule. Benson and DeMore[6] explained the formation of **3** in terms of a rearrangement mechanism first suggested by Slaugh et al.,[7] i.e., rearrangement of **5** by hydrogen migration of **6**, which, by vinyl migration, forms **7** (eq 2).

They interpreted the conversion of **6** to **7** in terms of an intermediate cyclopropylcarbinyl radical **8**, formed by intermolecular addition of the radical center to the C=C bond:

$$1 + 2 \longrightarrow \underset{\mathbf{5}}{(CH_3)_2CH{-}CH{=}\dot{C}H} \longrightarrow \underset{\mathbf{6}}{CH_3\overset{CH_2\cdot}{\overset{|}{C}}H{-}CH{=}CH_2} \longrightarrow \underset{\mathbf{7}}{CH_3{-}\overset{CH_2{-}CH{=}CH_2}{\overset{|}{C}}H\cdot} \quad (2)$$

$$\underset{\mathbf{6}}{H_3C\overset{CH_2}{\overset{/\ \backslash}{C}}H{-}CH_2\cdot} \longrightarrow \underset{\mathbf{8}}{} \longrightarrow \underset{\mathbf{7}}{} \quad (3)$$

Cyclopropylmethyl radicals readily undergo exothermic conversion to 3-butenyl radicals.[8]

This mechanism involves the intramolecular addition of a radical to the penultimate carbon atom in a terminal olefin. Normally radicals add preferentially to the terminal atoms of terminal olefins,[9] giving rise to secondary radicals that are more stable than terminal ones. However, the reverse usually seems to be the case in the cyclization of terminally unsatu-

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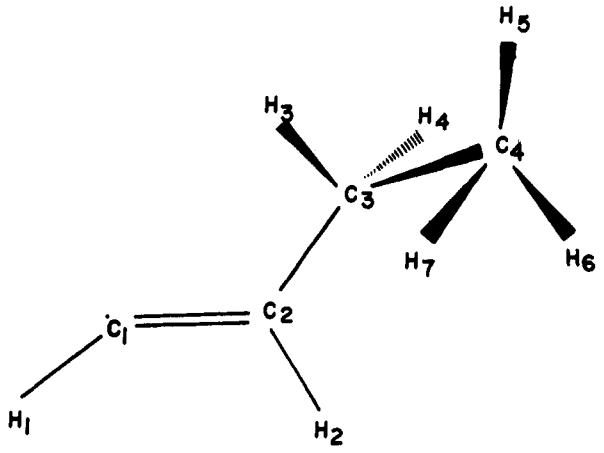
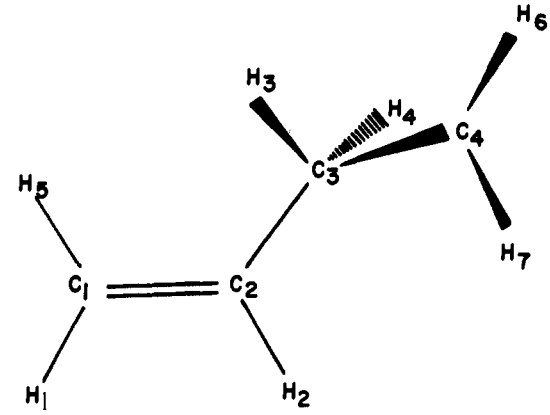


ΔH_f = 42.2

Bond length (Å)	Bond Angle (°)	Dihedral Angle (°)
C_1C_2= 1.304	$C_1C_2C_3$= 132.6	$C_1C_2C_3C_4$= 121.2
C_2C_3= 1.487	$C_2C_3C_4$= 119.8	$C_1C_2C_3H_3$= 3.9
C_3C_4= 1.495	$H_1C_1C_2$= 143.8	$C_2C_3C_4H_5$= 60.3
C_1H_1= 1.084	$H_2C_2C_1$= 114.5	$C_2C_3C_4H_6$= 180.0
	$H_3C_3H_4$= 102.2	$C_2C_3C_4H_7$= 299.7
	$H_6C_4H_7$= 105.4	

Figure 1. Calculated geometry and heat of formation (ΔH_f, kcal/mol at 25 °C) for **12**.

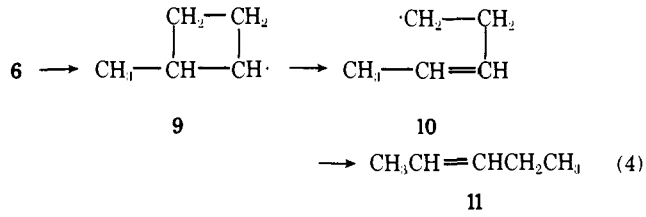


ΔH_f = 37.4

Bond length (Å)	Bond Angle (°)	Dihedral Angle (°)
C_1C_2= 1.327	$C_1C_2C_3$= 131.9	$C_1C_2C_3C_4$= 120.0
C_2C_3= 1.489	$C_2C_3C_4$= 120.6	$C_1C_2C_3H_3$= 5.9
C_3C_4= 1.454	$H_1C_1C_2$= 124.2	$C_2C_3C_4H_7$= 1.5
C_1H_5= 1.099	$H_2C_2C_1$= 116.0	
C_4H_6= 1.096	$H_3C_3H_4$= 101.3	
	$H_6C_4H_7$= 113.1	

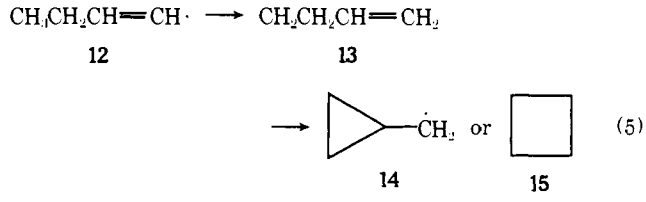
Figure 2. Calculated geometry and heat of formation (ΔH_f, kcal/mol at 25 °C) for **13**.

rated radicals by intramolecular addition.[8] This, in particular, generally seems to be the case[8,9] for 3-butenyl radicals that cyclize to cyclopropylmethyl radicals rather than cyclobutyl ones. Thus, in the case of **6**, there is no evidence for its conversion to 2-pentene (**11**) via **9** and **10** (eq 4). No entirely satisfactory explanation of this difference between the intra- and intermolecular additions seems to have been given.



(4)

We recently reported[10] a theoretical (MINDO/3[11]) study of the intramolecular addition of radicals to carbon-carbon multiple bonds. The results were in excellent agreement with experiment, particularly when a spin-unrestricted version (UMINDO/3[12]) of MINDO/3 was used. We have now used the same procedure to study the various reactions discussed above, the calculations being carried out for the simplest case, i.e., that involving the adduct **12** of ethyl radical with acetylene (eq 5). The only previous theoretical study in this area appears



(5)

to be one by Hehre,[13] of the conversion of **13** to **14** by the Roothaan-Hall (ab initio SCF) method using the STO-3G and 4-31G basis sets.

Theoretical Procedure

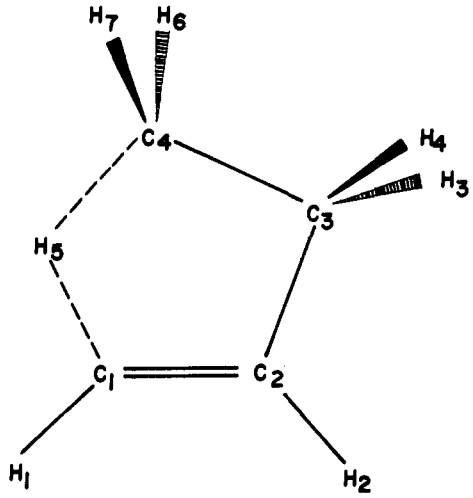
The calculations were carried out using a spin-unrestricted version (UMINDO/3[12]) of the MINDO/3 procedure[11] together with the associated DFP geometry program. All equilibrium geometries were found by minimizing the energy with respect to all geometrical variables, no assumptions being made. Minimum energy reaction paths (MERP) were determined by the usual reaction coordinate method,[14] the energy being minimized with respect to all other geometrical variables for successive increments in the reaction coordinate. The transition states, located approximately from the MERPs, were refined by minimizing the scalar gradient.[15] It was established that each such structures was a true transition state by diagonalizing the force constant matrix and thus determining that it had one, and only one, negative eigenvalue.[15]

Results and Discussion

The conformations of olefins follow rules similar to those for paraffins if a bent ("banana") bond model is used for C=C bonds. On this basis **12** should, like *n*-butane, exist in gauche and cis forms. We indeed found two corresponding minima on the MINDO/3 potential surface, that for the gauche conformer being the lower in energy by 1.7 kcal/mol. In the case of *n*-butane, MINDO/3 correctly predicts the gauche conformer to be the more stable. The calculated difference in energy between it and the trans conformer is also in good agreement with experiment (0.6 kcal/mol[16]).

The geometry and heat of formation calculated for gauche **12** are shown in Figure 1. The geometry corresponds closely to that expected on the basis of the MINDO/3 structures for vinyl radical (R(CC), 1.291 Å; angle (HCC), 146.0°) and ethane (R(CC), 1.486 Å). No experimental study of the structure of **12** has as yet been reported.

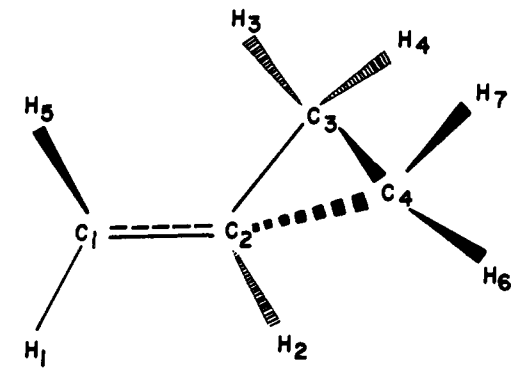
Figure 2 shows the equilibrium geometry and heat of formation calculated for allylcarbinyl radical **13**. This again has a gauche conformation, as expected and in agreement with an ESR study by Edge and Kochi.[17] Note that the hydrogen atoms H_6 and H_7 prefer to eclipse the C_2C_3 bond. This result



ΔH_f = 68.9

Bond Length (Å)	Bond Angle (°)	Dihedral Angle (°)
C_1C_2= 1.332	$C_1C_2C_3$= 110.8	$C_1C_2C_3C_4$= 0.0
C_2C_3= 1.499	$C_2C_3C_4$= 103.4	$C_1C_2C_3H_5$= 0.0
C_3C_4= 1.502	$H_1C_1C_2$= 137.8	$C_2C_3C_4H_7$= 114.3
C_1H_1= 1.092	$H_2C_2C_1$= 127.1	
C_4H_6= 1.107	$H_3C_3H_4$= 103.0	
C_1H_5= 1.307	$H_6C_4H_7$= 107.7	
C_4H_5= 1.318	$C_3C_4H_5$= 98.5	
	$C_4H_5C_1$= 102.0	
	$H_5C_1C_2$= 125.2	

Figure 3. Calculated geometry and heat of formation (ΔH_f, kcal/mol at 25 °C) for the transition state for **12** → **13**.



ΔH_f = 50.3

Bond Length (Å)	Bond Angle (°)	Dihedral Angle (°)
C_1C_2= 1.362	$C_1C_2C_3$= 132.4	$C_1C_2C_3C_4$ =100.7
C_2C_3= 1.492	$C_2C_3C_4$= 81.3	$H_3C_3C_2C_1$ = 16.4
C_3C_4= 1.452	$C_3C_2C_4$= 48.5	$H_7C_4C_3C_2$ =103.3
C_2C_4= 1.918	$H_1C_1C_2$= 123.5	$H_5C_1C_2C_3$ = 7.6
	$H_2C_2C_1$= 114.1	$H_2(C_1C_2C_3)$=171.5
	$H_3C_3H_4$= 105.5	$C_3(H_6C_4H_7)$=161.2
	$H_6C_4H_7$= 111.3	$C_2(H_1C_1H_5)$=174.4

Figure 4. Calculated geometry and heat of formation (ΔH_f, kcal/mol at 25 °C) for the transition state for **13** → **14**.

is consistent with the ESR findings of Edge and Kochi but not with the ab initio calculations reported by Hehre.[13] We found the barrier to rotation about the C_3C_4 bond to be 0.5 kcal/mol.

The transition state for interconversion of the gauche conformers of **12** and **13** was located by using the C_1-H_5 interatomic distance as a reaction coordinate and refined in the usual way.[15] Its heat of formation and structure are shown in Figure 3. Note that the migrating hydrogen atom is approximately midway between the two terminal carbon atoms, each CH distance being ca 1.33 Å. The calculated unpaired electron densities on C_1 and C_4 (0.41 and 0.44 e, respectively) indicate that the open shell molecular orbital is almost equally localized on these atoms.

The energy of the calculated transition state lies 26.5 kcal/mol above 1-butenyl radical. This potential barrier height is greater than the activation energy (17.1 kcal/mol) reported by Watkins and O'Deen[5] for the corresponding 1,4 intermolecular hydrogen migration in 3-methyl-1-butenyl radical (**5**), but the difference is within the possible limits of error of MINDO/3.[11]

The calculated heat of isomerization of **12** to **13** (−4.9 kcal/mol) is in reasonable agreement with that (ca. −10 kcal/mol) estimated from thermochemical data.[18]

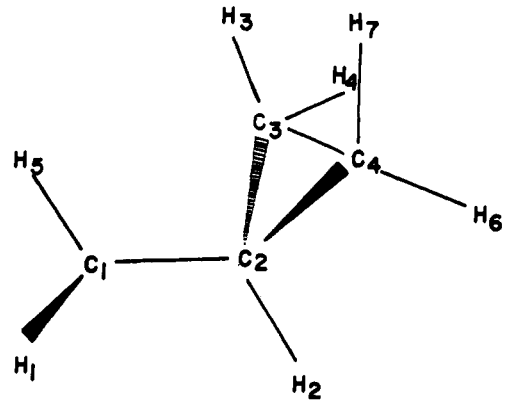
The conversion of **13** to **14** was next studied, using the $C_2C_3C_4$ bond angle (θ) as the reaction coordinate. The transition state ($\theta \sim 81°$) located in this way was refined by minimizing the scalar gradient of the energy.[15] The final structure and heat of formation are shown in Figure 4. We established that this was a true saddlepoint by showing that the corresponding Hessian (force constant) matrix had one and only one negative eigenvalue (cf. ref 15).

A further decrease in θ, followed by geometry optimization, led directly to **14**. A detailed search of the potential surface failed to reveal any path for the skeletal rearrangement of **13** (i.e., $C_1{=}C_2C_3C_4\cdot \rightarrow C_1{=}C_2C_4C_3\cdot$) of lower energy than that via **14** or, indeed, any direct path involving a single transition state. Our calculations therefore imply that the easiest path for the vicinal shift in **13** is a two-step process involving **14** as a stable intermediate, in agreement with the mechanism suggested by Benson and De More and with deuterium labeling studies by Montgomery and Matt.[19] The heat of formation calculated for the transition state for **13** → **14** is much less positive than that for **12** → **13**, implying that the latter step is rate determining for the overall rearrangement.

Our studies[10] of intermolecular addition of radicals to olefins indicated that while the radicals have product-like geometries in the transition states, those of the olefins are reactant-like, a conclusion apparently supported by measurements of isotope effects. The structure calculated here for the transition state (**13** → **14**) (Figure 4) shows a similar dichotomy. Thus, the C_1C_2 bond length is only 0.03 Å greater than in **13** and the $H_2C_2C_3$ plane is tilted only 8° from its original position, whereas the radical center (C_4) is now pyramidal, the C_3C_4 bond being tilted 29° out of the plane defined by $H_6C_4H_7$.

The calculated activation barrier for **13** → **14** (12.9 kcal/mol) is less than Hehre's[13] (17.3 kcal/mol) but probably still too high. While no experimental value is available, the ESR spectrum of **13** cannot be observed at temperatures above −120 °C, implying that the rate of rearrangement is then greater than the rate of removal of radicals by combination or disproportionation. The activation energy for **13** → **14** is then probably in the range 8-10 kcal/mol.[21]

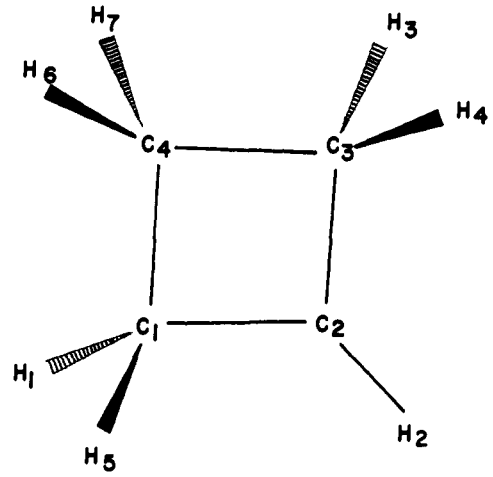
The geometry and heat of formation calculated for **14** are shown in Figure 5. It will be seen that it has a bisected structure, in agreement with ESR studies.[17,20] Our calculations correctly predict **14** to be less stable than **13**, but the calculated difference in heat of formation (0.5 kcal/mol) is less than that observed (5 kcal/mol[23]).



ΔH_f = 37.9

Bond Length (Å)	Bond Angle (°)	Dihedral Angle(°)
C_1C_2= 1.440	$C_1C_2C_3$= 127.1	$H_5C_1C_2C_3$ = 41.4
C_2C_3= 1.521	$C_2C_3C_4$= 61.1	$H_1C_1C_2H_2$ = 13.7
C_3C_4= 1.480	$C_3C_2C_4$= 58.1	$H_2C_2C_1H_5$ = 176.4
C_2C_4= 1.526	$H_1C_1C_2$= 121.7	$C_1(C_3C_2C_4)$= 134.0
	$H_2C_2C_1$= 109.7	$C_2(H_1C_1H_5)$= 166.8
	$H_5C_1H_1$= 112.6	
	$H_6C_4H_7$= 107.7	

Figure 5. Calculated geometry and heat of formation (ΔH_f, kcal/mol at 25 °C) for **14.**

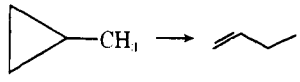


ΔH_f = 26.7

Bond Length (Å)	Bond Angle(°)	Dihedral Angle(°)
C_1C_2= 1.486	$C_1C_2C_3$= 93.8	$C_1C_2C_3C_4$= 0.0
C_2C_3= 1.486	$C_2C_3C_4$= 88.0	$H_2C_2C_1C_3$= 177.5
C_3C_4= 1.531	$C_2C_1C_4$= 88.0	
C_1C_4= 1.531	$H_2C_2C_1$= 133.1	
	$H_1C_1H_5$= 103.9	

Figure 6. Calculated geometry and heat of formation (ΔH_f, kcal/mol at 25 °C) for **15.**

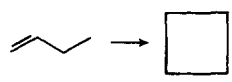
Such a difference would be expected by analogy with the heat of isomerization of the parent hydrocarbons, i.e.:



While no accurate thermochemical data seem to be available for methylcyclopropane, the results in Table I indicate that the MINDO/3 value for the heat of isomerization is probably too positive by 5 kcal/mol.

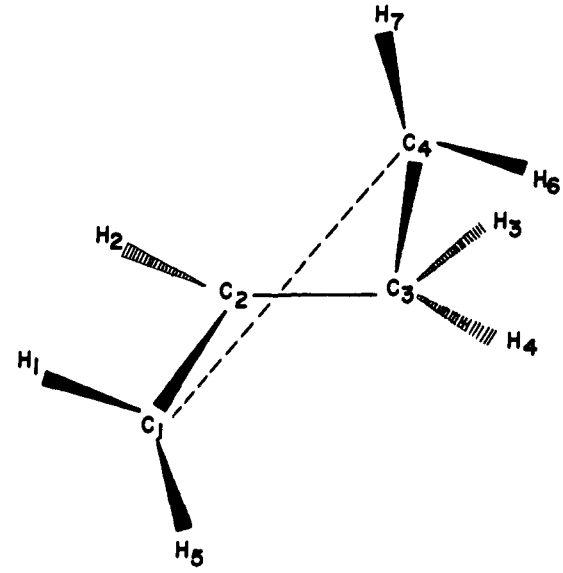
Our final calculation was concerned with the alternative mode of cyclization of **13,** to cyclobutyl radical **15.** Figure 6 shows the geometry and heat of formation calculated for the latter. It will be seen that MINDO/3 predicts **15** to be more stable than **14** by 11.2 kcal/mol. While this value is probably too large,[23] it seems very unlikely that the conversion of **13** to **15** can be appreciably more exothermic than that of **13** to **14.** Failure to observe the former reaction therefore implies that this is one of the exceptional[10] radical addition reactions that do not lead to the most stable possible products.

The transition state for **13** → **15** was located without difficulty by taking the length of the forming (C_1C_4) bond as the reaction coordinate. Figure 7 shows its refined[15] geometry and calculated heat of formation. It will be seen that the latter is more positive by no less than 17.1 kcal/mol than that of the transition state for **13** → **14.** Indeed, since MINDO/3 probably gives too negative a value for the heat of reaction for **13** → **15,** judging by data[11] for the corresponding reaction of the parent hydrocarbons (Table I), i.e.,



the calculated activation energy is probably too low. It is therefore not surprising that cyclization of **13** leads to a three-membered ring.

The reason for this remarkably large difference becomes



ΔH_f = 67.4

Bond Length(Å)	Bond Angle(°)	Dihedral Angle(°)
C_1C_2= 1.377	$C_1C_2C_3$= 110.4	$C_1C_2C_3C_4$= 23.0
C_2C_3= 1.489	$C_2C_3C_4$= 90.4	$H_5C_1C_2C_3$ = 53.6
C_3C_4= 1.488	$H_1C_1H_5$= 107.2	$H_1C_1C_2C_3$ =152.8
C_1C_4= 2.064	$H_6C_4H_7$= 108.9	$H_2C_2C_1H_1$ = 2.9
		$H_2(C_1C_2C_3)$ =154.6
		$C_3(H_6C_4H_7)$ =148.0
		$C_2(H_1C_1H_5)$ =146.9

Figure 7. Calculated geometry and heat of formation (ΔH_f, kcal/mol at 25 °C) for the transition state for **13** → **15.**

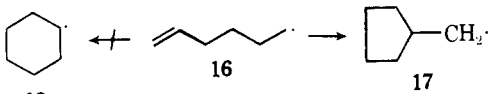
Table I. Calculated and Observed Heats of Formation

compd	heat of formation[a] calcd (MINDO/3)	obsd	error
	1.0	−0.2	1.2
	8.7	12.7	−4.0
cis	−2.0	1.3	−3.3
	−5.1	6.8	−11.9[b]

[a] Kilocalories/mole at 25 °C; data from ref 11. [b] Since MINDO/3 underestimates eclipsing interactions in ethane by 2 kcal/mol,[11] 8 kcal/mol of the discrepancy in cyclobutene is probably due to this error. Since two such interactions disappear in cyclobutyl radical, the MINDO/3 heat of formation for this is probably too negative by ca. 8 kcal/mol rather than 12.

apparent if the structures of the two transition states (Figures 4 and 7) are examined in the light of our earlier[10] calculations for the addition of radicals to olefins. In the transition states for the latter, the olefin moieties were almost unperturbed and the approaching radical lay close to the axis of one of the 2p atomic orbitals forming the π bond. While the transition state for **13** → **14** has a similar geometry, as we have already pointed out, that for **13** → **15** does not. In the latter, the radical approaches the double bond from one side and the double bond itself is twisted, distortions enforced by the geometry and electronic requirements of the system. These distortions must of course greatly increase the total energy. Thus, although the strain energies of **14** and **15** are probably similar, those of the transition states leading to them are not. The extra strain energy in that leading to **15** accounts for the failure for such products to be formed by cyclization of allylcarbinyl radicals.

Similar though smaller strain effects should also occur in analogous cyclizations of higher homologues of **13**, leading to larger rings. This indeed seems to be the case. Thus, intramolecular cyclization of 4-pentenyl (**16**) gives cyclopentylmethyl (**17**) rather than cyclohexyl (**18**).[8]



18 16 17

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Supplementary Material Available: Tables of calculated (MINDO/3) cartesian coordinates for **12** → **13**, **13** → **14**, and **13** → **15** (2 pages). Ordering information is given on any current masthead page.

References and Notes

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