and diisopropyl peroxydicarbonates were gifts from PPG Industries, Inc., Chemical Division and used without further purification. Ethylene, isobutylene, butadiene, and cyclopropane were from Matheson and propylene from Baker Chemical Co. Di-*tert*-butyl peroxide was obtained from the Shell Chemical Co. and washed and redistilled at reduced pressure prior to use. Triethylsilane was obtained from Columbia Organic Chemical Co. Other acyl peroxides used in this study were prepared previously.[2]

2-Bromoethyl *n*-butyl ether was prepared from the mono-*n*-butyl ether of ethylene glycol and phosphorus tribromide by the method given for the ethyl ether[56] (bp 170–171°).

2-Bromoethyl ethyl carbonate was prepared from 2-bromoethanol and ethyl chloroformate using the general method of Ritchie for the preparation of unsymmetrical dialkyl carbonates[57] (mp 7–10°).

2-Bromo-1-phenylpropane was prepared by treatment of the corresponding alcohol with phosphorus tribromide[58] (bp 100–101° (10 mm), lit. 114° (21 mm)).[58]

Acknowledgment. We wish to thank the National Science Foundation for financial support of this work and PPG Industries, Inc. for generous samples of the dialkyl peroxydicarbonates used in this study.

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Mechanisms of Free-Radical Reactions. I. Interconversion of Homoallyl and Cyclopropylcarbinyl Free Radicals

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Abstract: A section of the C_4H_7 potential surface connecting and including the homoallyl and cyclopropylcarbinyl free radicals has been investigated by *ab initio* molecular orbital theory. Both isomers are stable minima, the former being the lower in energy, and are connected by a small but finite activation barrier.

Concerted interconversions between stable hydrocarbon free radicals generally require moderate activation energies; low enough for the processes to occur facilely at ordinary temperatures, and yet sufficiently high to allow for characterization of individual species by conventional spectroscopic and chemical methods.[2] Significant progress has been made in recent years both toward the synthesis of specific precursor free radicals and in the routine interpretation of electron spin resonance (esr) spectra of increasing complexity,[3] and it would seem to this author that radical systems may soon provide a unique opportunity for the study of organic reaction mechanisms. Nonempirical theoretical techniques applicable to the study of the energetics of radicals have also evolved impressively during the past decade. Although their applications have for the most part thus far been restricted to studies of equilibium geometry[4] and conformational behavior,[5] indications are that meaningful results might be obtained from explorations of reaction potential surfaces. In this paper we report an application of *ab initio* molecular orbital theory to a section of the C_4H_7 potential surface including and connecting the homoallyl and cyclopropylcarbinyl free radicals. Our primary intent is to establish whether or not the individual species are stable minima on the C_4H_7 surface, and if so the nature of the transition state connecting them. Comparison of our findings with the recent esr results of Krusic and coworkers[6] is inevitable, and it is hoped that such might form a guide for later theoretical studies where experiments have not as yet been performed or have led to ambiguous findings. We shall also be interested in a comparison of the energetic surface for homoallyl–cyclopropylcarbinyl interconversion with our previously reported studies on the analogous carbocationic species.[7] In this previous work it was shown that the distant interaction of a formally vacant orbital with an area of high electron density led to a collapse of the acyclic homoallylic structure to cyclopropylcarbinyl. It will be interesting to probe the consequences of the related (radical center–ethylene π system) interaction.

Methods. We employ standard single determinant

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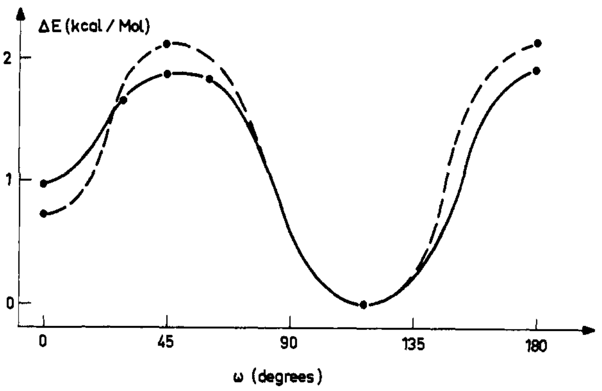


Figure 1. Potential for rotation about the central bond in the homoallyl free radical: (——) STO-3G, (- - -) 4-31G.

Table I. STO-3G Geometry for Gauche Homoallyl Free Radical[a]

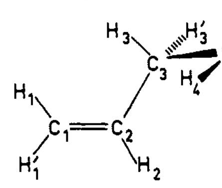
$r(C_1C_2) = 1.311$ Å	$r(C_2C_3) = 1.530$ Å
$r(C_3C_4) = 1.526$ Å	
$\angle(C_1C_2C_3) = 124.9°$	$\angle(C_2C_3C_4) = 111.8°$
$\angle(C_3C_4H_{44'})^b = 154.0°$	$\omega(C_1C_2C_3C_4)^c = 116.6°$

[a] A full geometry search has been performed on the tabulated parameters; all others have been assigned the following values: $r(C_1H_1)$, $r(C_1H_{1'})$, $r(C_2H_2)$, 1.08 Å; $r(C_3H_3)$, $r(C_4H_4)$, 1.09 Å; $\angle(H_1C_1C_2)$, $\angle(H_{1'}C_1C_2)$, $\angle(H_2C_2C_1)$, 120°; $\angle(H_3C_3H_{3'})$, 109.5°; $\angle(H_4C_4H_{4'})$, 116°; the plane formed by carbon 3 and hydrogens 3 and 3′ is constrained to bisect the angle $C_2C_3C_4$. [b] $C_4H_{44'}$ is the bisector of the plane formed by carbon 4 and hydrogens 4 and 4′. The dihedral angle $C_2C_3C_4H_{44'}$ is allowed to take either cis (0°) or trans (180°) conformations. The cis is favored; see text. [c] Dihedral angle.

ab initio molecular orbital theory throughout (spin unrestricted method[8]) utilizing the STO-3G[9] and 4-31G[10] Gaussian basis sets. The former, a minimal basis, has been shown to be especially suitable for the calculation of molecular equilibrium geometries, as it is relatively inexpensive to apply and has been extensively tested.[4] It is primarily for this purpose that it is employed here. The STO-3G functions have, however, a known tendency to overestimate the stability of cyclic molecules with respect to their acyclic counterparts,[11] and for this reason we have recalculated several points on the STO-3G potential surface using the extended 4-31G basis set, functions flexible enough to readily account for anisotropic molecular environments. Direct geometry optimization using the 4-31G basis is at present economically unfeasible. All calculations have been performed using the GAUSSIAN 70 series of programs.[12]

Results and Discussion

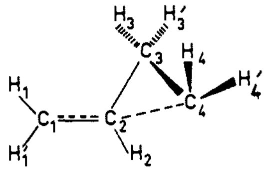
Homoallyl free radical is found to prefer a gauche carbon skeletal arrangement (I), the optimum STO-3G



I

geometrical parameters for which are presented in Table I. The reported geometry deviates only slightly from what one might predict based only on the optimum STO-3G structures for ethylene[4a] ($r(C{=}C) = 1.305$ Å) and the ethyl free radical[4a] ($r(C{-}C) = 1.516$ Å), and stands in striking contrast to our earlier studies on the homoallyl cation.[7] Note that the hydrogens H_4 and $H_{4'}$ prefer to stagger the C_2C_3 bond rather than to eclipse it, consistent with previous investigations on the ethyl free radical[4a] but contrary to the esr findings of Edge and Kochi,[6c] who interpret the observed temperature-dependent broadening of the lines associated with the α (radical site) protons in terms of an eclipsed arrangement. A second minimum was located for the homoallyl free radical corresponding to a cis carbon skeleton ($\omega(C_1C_2C_3C_4) = 0°$), but this proved to be 0.7 kcal/mol less stable than the gauche form, and separated by a potential barrier (gauche to cis) of approximately 2.1 kcal/mol (Figure 1). With regard to the conformation about the central carbon–carbon bond, the theory is in qualitative agreement with the recent work of Edge and Kochi.[6c] These authors observe no lie broadening associated with the β protons, and hence conclude that rotation about C_β–C_γ is essentially unhindered.

In order to investigate the rearrangement of homoallyl free radical to cyclopropylcarbinyl, we have chosen the $C_2C_3C_4$ angle (α) as a reaction coordinate (ranging from 111.8° in gauche homoallyl to approximately 60° in cyclopropylcarbinyl) and have performed geometry optimization *at the same level as detailed above* for homoallyl free radical for intermediate values of α of 90, 80, and 70°. The $\alpha = 80°$ form is the highest energy point on the calculated pathway, and hence within the limits of our geometrical search represents the transition state structure (II), geometrical parameters



II

of which are presented in Table II. Note that the C_4 hydrogens have undergone inversion (from their arrangement in the homoallyl free radical) and now

Table II. STO-3G Geometry for the Transition State to Homoallyl–Cyclopropylcarbinyl Rearrangement[a]

$r(C_1C_2) = 1.400$ Å	$r(C_2C_3) = 1.516$ Å
$r(C_3C_4) = 1.499$ Å	
$\angle(C_1C_2C_3) = 124.3°$	$\angle(C_2C_3C_4) = 80°^b$
$\angle(C_3C_4H_{44'})^c = 163.8°$	$\omega(C_1C_2C_3C_4)^d = 95.2°$

[a] Geometrical constraints are the same as those for the gauche homoallyl free radical; see footnote *a* of Table I. Twisting around the C_1C_2 bond to allow hydrogens H_1 and $H_{1'}$ to become out of plane was permitted, but found not to occur to a significant extent. [b] Assigned. [c] $C_4H_{44'}$ is the bisector of the plane formed by carbon 4 and hydrogens 4 and 4′. [d] Dihedral angle.

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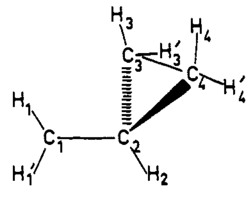
eclipse the hydrogens on C_3, and that the C_1C_2 bond length has considerably elongated (from 1.311 Å in homoallyl), while the separation between carbons 2 and 4 has diminished to 1.938 Å (from 2.530 Å in the gauche homoallyl free radical). The carbon skeleton has now taken a nearly orthogonal arrangement, in preparation for closure to a three-membered ring.

The geometry of the bisected form of cyclopropylcarbinyl (III) has been only partially optimized, and is presented in Table III. Such a structure is found to be 1.4 kcal/mol more stable than the corresponding orthogonal form in qualitative agreement with experimental (esr) measurements[6] which suggest a rotational barrier of <3 kcal/mol,[6b] and with previous theoretical findings.[5]



III

Table III. STO-3G Geometry for Bisected Cyclopropylcarbinyl[a]

$r(C_1C_2) = 1.499$ Å	$\angle(C_1C_2C_{34})^b = 119.4°$

[a] Bond lengths C_1H_1 and $C_1H_{1'}$ and bond angles $H_1C_1C_2$ and $H_{1'}C_1C_2$ taken from the optimum STO-3G structure for the ethyl free radical, ref 4a; remaining bond lengths and angles from the STO-3G structure for cyclopropane, ref 11. [b] C_2C_{34} is the bisector of the plane formed by carbons 2, 3, and 4

Extended basis 4-31G calculations have been performed on the gauche homoallyl and bisected cyclopropylcarbinyl potential minima, as well as for the intermediate α = 90, 80, and 70° structures. The resulting energies (relative to the gauche homoallyl free radical) are presented in Table IV along with the corresponding STO-3G values. Figure 2 displays these graphically as a function of our reaction coordinate α.

Table IV. Theoretical Energy Data for the Isomerization of Homoallyl to Cyclopropylcarbinyl Free Radical (kcal/mol)

ΔE^a	STO-3G	4-31G
Gauche homoallyl (I)	0	0
(II) α = 90°	7.9	10.7
(II) α = 80°	14.1	17.3
(II) α = 70°	5.3	15.8
Bisected cyclopropylcarbinyl (III)	−7.5	8.6

[a] A positive entry indicates the species to be less stable than gauche homoallyl free radical; a negative entry, more stable.

Both the STO-3G and 4-31G methods predict the two species, homoallyl and cyclopropylcarbinyl free radicals, to be minima on the C_4H_7 potential surface, in agreement with esr observations.[6a] Furthermore, the position of the transition state along our chosen reaction coordinate is predicted to be approximately the same for the two theoretical schemes. The STO-3G basis finds cyclopropylcarbinyl to be the more stable species (7.5 kcal/mol lower in energy than homoallyl free radical); in contrast to this 4-31G predicts an opposite ordering of stabilities. The quantitative difference in the predictions of the two methods is readily understandable in terms of previous experience and is thought to be primarily due to the inability of the minimal functions to adequately describe anisotropic molecular environments. Thus STO-3G finds that cyclopropane is 3.7 kcal/mol more stable than propene, while the 4-31G set predicts the latter to be of lower energy (by 13.2 kcal/mol) in agreement with experiment.[11] A more relevant comparison perhaps, is that between methylcyclopropane and gauche 1-butene. Here again the minimal basis energetically favors the cyclic molecule (by 6.8 kcal/mol), and again application of 4-31G reverses the ordering making the acyclic 1-butene 11.1 kcal/mol lower in energy.[13] Although meaningful direct energy comparisons with the STO-3G functions are obviously unsatisfactory,[14] it may be argued that the method provides a useful tool for locating equilibrium and transition state structures alike. The defects inherent to the STO-3G minimal basis seem fairly regular, and hence predictable, and one might hope that useful information may be derived from molecular potential surfaces computed at this level.

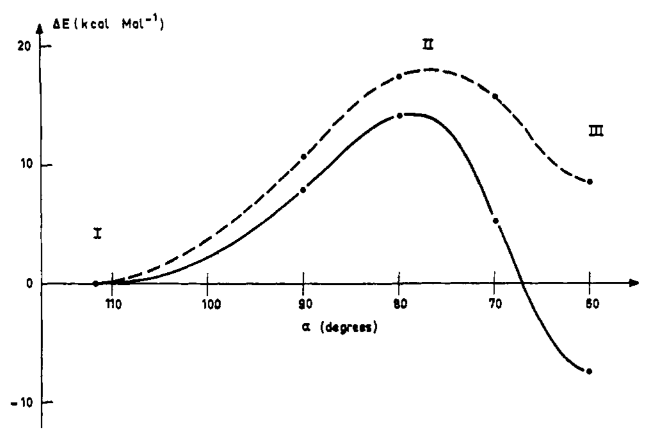


Figure 2. Interconversion of the homoallyl and cyclopropylcarbinyl free radicals: (——) STO-3G, (- - -) 4-31G.

The extended 4-31G calculations predict the homoallyl free radical to be 8.6 kcal/mol more stable than cyclopropylcarbinyl, in qualitative agreement with, but somewhat overestimating the observed difference of 5.1 kcal/mol.[15,16] An activation energy of ≃17.3 kcal/mol is required for the conversion of homoallyl to cyclopropylcarbinyl; activation required in the reverse direction is ≃8.7 kcal/mol. Experimental data are lacking.

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(14) It may be noted, however, that certain types of energy comparison are well described even at the minimal basis level. For a general discussion, see W. J. Hehre, R. Ditchfield, L. Radom, and J. A. Pople, *J. Amer. Chem. Soc.*, **92**, 4796 (1970); L. Radom, W. J. Hehre, and J. A. Pople, *ibid.*, **93**, 289 (1971).

(15) Calculated from the heat of formation of cyclopropylcarbinyl free radical ($\Delta H_f°$ (298°) = 51.1 ± 1.6 kcal/mol: D. F. McMillen, D. M. Golden, and S. W. Benson, *Int. J. Chem. Kinet.*, **3**, 359 (1971)), and that of homoallyl free radical ($\Delta H_f°$ (298°) = 46.0 kcal/mol: A. S. Gordon, S. R. Smith, and C. M. Drew, *J. Chem. Phys.*, **36**, 824 (1962)).

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Chemical and Electrochemical Reduction of 1,2-Dihalobenzocyclobutene[1]

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Received July 17, 1972

Abstract: The treatment of 1,2-dibromobenzocyclobutene with an excess of solvated electrons or with biphenyl radical anion results in the formation of benzocyclobutene. Benzocyclobutene is proposed to arise by the intermediate benzocyclobutadiene radical anion or dianion. Polarographic, cyclic voltammetric, and controlled potential electrolytic reduction studies of the generation of benzocyclobutadiene from the corresponding dihalide indicate dimerization to be faster than further reduction to benzocyclobutadiene radical anion.

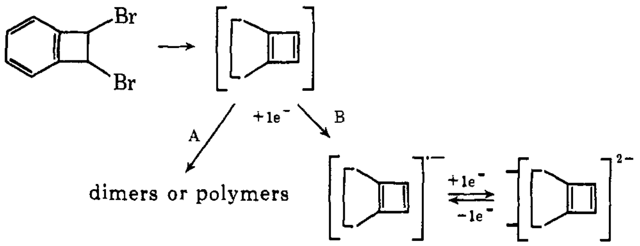
The cleavage of carbon–halogen bonds upon treatment with naphthalene or biphenyl radical anion solutions is well documented.[2-11] We recently reported on an attempt to extend this reaction toward the generation of reactive neutral unsaturated hydrocarbons.[1] The hope was that, in the presence of excess electrons, the neutral hydrocarbon would be reduced to its radical anion in a diffusion-controlled process. The radical anion in turn might be stable enough to allow its study by epr.

We wish to present our results on the treatment of 1,2-dihalobenzocyclobutene with solutions of solvated electrons in ethereal solvents and with naphthalene and biphenyl radical anions. We also studied the electrochemical reduction of the dihalides to examine the possibility that the reduction potential of benzocyclobutadiene might be found. Also, the 1,2-dihalobenzocyclobutenes were reduced in the presence of $MgBr_2$ with biphenyl radical anion.

Results

The initial attempts to generate the benzocyclobutadiene radical anion involved the reduction of *trans*-1,2-dibromobenzocyclobutene with ethereal solutions of solvated electrons. The solution of alkali metals in polyethereal solvents, giving rise to blue solutions of solvated electrons in concentrations of up to $1 \times 10^{-2}\ M$, has been extensively investigated,[12-16] Reduction of the dihalide was expected to give the very reactive benzocyclobutadiene as has been demonstrated by Cava using zinc as a reducing agent.[17] This could then dimerize, as shown in Scheme I, or it could be reduced to the radical anion or dianion in a diffusion controlled process.

Scheme I



Solutions of solvated electrons were prepared at −78° under high vacuum in one side of a tube of H-design (see Figure 2) which has an epr side arm attached. The concentration of solvated electrons was in large excess over that of the benzocyclobutene dihalide, which was contained in the other side of the double tube. Upon treatment of the dihalide with excess solvated electrons, a paramagnetic species resulted immediately. The paramagnetic species displayed the temperature dependence shown in the epr spectrum in Figure 1. At temperatures lower than −50°, the epr spectrum consisted of approximately 65 lines with apparent coupling constants of 7.60, 5.75, 5.25, and 1.45 G for four sets of two equivalent pro-

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