

orientation of the imidazole molecule in the imidazole-water dimer is quite flexible with respect to rotation of imidazole about its principal axis and about the intermolecular O-N line. The imidazole-water intermolecular potential surface resembles the pyrimidine-water surface in the region where pyrimidine is the proton acceptor molecule.

(5) Pyrrole forms stronger hydrogen bonds through its  $\pi$  electron system than ethylene, as indicated by the stabilization energies of 1.5 and 0.5 kcal/mol for the pyrrole-water and ethylene-water dimers, respectively. The most stable pyrrole-water  $\pi$  dimer is one in which water is a double proton donor, with  $\pi$  hydrogen bond formation occurring at the carbon atoms C<sub>3</sub> and C<sub>4</sub> and not at the nitrogen. The surrounding intermolecular surface is relatively flat, indicating that there is considerable flexibility in the orientation of the hydrogen bonded molecules.

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 (18) The intermolecular coordinates for the pyrrole-HF dimer are  $\theta_1 = 34^\circ$ ,  $\theta_2 = 120^\circ$ ,  $\chi_2 = 90^\circ$ ,  $\phi = 180^\circ$ , and  $R = 3.97 \text{ \AA}$ .  
 (19) The amount of charge transfer in dimer C is very small (0.006e), as expected when hydrogen bonds are weak. However, the standard pattern of electron density changes upon hydrogen bond formation is discernible. Specifically, the electron densities of the oxygen atom in the proton donor molecule and of the carbon atoms C<sub>3</sub> and C<sub>4</sub> increase, while those of the hydrogen bonded protons decrease.  
 (20) In these dimers, the water molecule is perpendicular to the pyrrole ring at the C<sub>2</sub>-C<sub>3</sub> and N<sub>1</sub>-C<sub>2</sub> bonds, respectively. These dimers were optimized with respect to the distance between the oxygen atom and the midpoints of these bonds. The optimized distances are about 3.55 Å.  
 (21) This dimer has optimized intermolecular coordinates  $\theta_1 = 45^\circ$ ,  $\theta_2 = 176^\circ$ , and  $R = 2.94 \text{ \AA}$ .

## Ground States of Molecules. 48. MINDO/3 Study of Some Radical Addition Reactions<sup>1</sup>

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**Abstract:** The potential surfaces for the additions of methyl radicals to ethylene, acetylene, propene, and allene have been studied, using MINDO/3. The calculated activation energies agree well with experiment, as do the predicted points of attack in propene and allene. The transition states have unusual structures, being reactant-like except for the attacking methyl which has a product-like pyramidal geometry. This accounts for apparent contradictions in the experimental evidence.

The addition of alkyl radicals to multiple bonds is a process which has attracted much attention.<sup>2</sup> These reactions take place rapidly, having rate constants of the order of  $10^3$ - $10^4 \text{ L mol}^{-1} \text{ s}^{-1}$  at ambient temperatures,<sup>2,3</sup> activation energies<sup>4</sup> in the range  $6 \pm 2 \text{ kcal/mol}$ , and Arrhenius preexponential factors<sup>4</sup> between  $10^6$  and  $10^9$ . While polar and steric effects play a role in determining the rate and direction of addition to a given double or triple bond, the determining factor in most cases seems to be the exothermicity of the reaction. In particular, the direction of addition to a given double or triple bond is usually that which leads to more stable product.

While the stereochemistry of these reactions has been extensively studied,<sup>5</sup> there is still uncertainty concerning their detailed mechanisms. It was formerly thought that the reagents first combine to form a  $\pi$  complex, or that a structure of this kind might represent the transition state, but arguments based on simple LCAO-MO theory make this unlikely.<sup>6</sup> The ex-

perimental evidence currently available seems to suggest that the optimum mode of approach of the alkyl group is along a line through one of the terminal atoms of the multiple bond and perpendicular, or almost perpendicular, to the nodal plane of the  $\pi$  MO involved in the reaction.<sup>7</sup> Toward the end of the reaction, there must of course be a reorganization of the atom undergoing attack from trigonal to tetrahedral geometry (or digonal to trigonal in the case of addition to a triple bond). The question then arises, what point along this path corresponds to the transition state? If the transition state occurs early, the unsaturated molecule will more or less retain its initial geometry and the transition state will be reactant-like, whereas a late transition state will have a structure similar to that of the product.

Studies<sup>8</sup> of secondary deuterium isotope effects in the additions of methyl radicals to olefins, and to deuterated olefins, in the gas phase suggest that the transition states are reac-

tant-like. However, kinetic data<sup>9</sup> for the reverse reactions seemed to lead to the opposite conclusion, implying that the radical and olefin are tightly bound in the transition state. The latter conclusion is supported by calculations by Bloor et al.,<sup>10</sup> which show that the rates of addition of methyl and ethyl radicals to a variety of olefins correlate well with the calculated localization energies of the latter.

The addition of methyl radical to ethylene has been studied theoretically by Basilevsky and Chelenov,<sup>11</sup> using a  $\pi$  approximation with corrections for changes in hybridization of the unsaturated carbon atoms, and by Hoyland,<sup>12</sup> using MINDO/2.<sup>13</sup> Both these calculations led to good estimates of the activation energy and Hoyland<sup>12</sup> also studied the addition of methyl radical to butadiene with comparable success. The transition state in each case was predicted to be reactant-like in structure.

The methods used in these calculations were, however, rather primitive and they referred in any case to only two reactions. The only other quantitative study of methyl addition seems to be one reported by Bonačić-Koutecký et al.<sup>14</sup> using a minimum basis set Roothaan-Hall *ab initio* treatment. These authors state, however, that their calculated activation energies were far too large and indeed they failed to quote them. Also, although they claimed to have optimized the geometries of their transition states, no results were given, and their calculations for methyl apparently referred only to addition to mono- and trifluoroethylene. All these studies have therefore left much to be desired.

Some years ago we reported the development of a final version (MINDO/3<sup>15</sup>) of the MINDO method and since then very extensive tests have shown it to give good results for a very wide variety of chemical properties and types of reaction.<sup>16</sup> Here we report its application to the addition of methyl radicals to various hydrocarbons containing multiple bonds.

### Theoretical Procedure

The MINDO/3 method has been discussed in detail.<sup>15</sup> The calculations reported here were carried out using the standard parameters.<sup>15</sup> The geometries of molecules were found by minimizing the total energy with respect to *all* geometrical variables using a program based on the Davidson-Fletcher-Powell (DFP) algorithm.<sup>17</sup> Transition states were located approximately by the usual reaction coordinate procedure<sup>16</sup> and then refined by minimizing the norm of the gradient, as suggested by McIver and Komornicki.<sup>18</sup> Transition states can be distinguished<sup>18</sup> from other stationary points by the fact that the second derivative (Hessian) matrix has one, and only one, negative eigenvalue. This test was applied in each case.

Previous MINDO/3 calculations here for open shell species have mostly used the "half-electron" (HE) approximation.<sup>19</sup> However, difficulties arise in this case because the resulting wave function is not variationally optimized<sup>20</sup> and is consequently not invariant for small changes in the geometry. In the usual MINDO/3 procedure, derivatives of the energy are found either analytically or by finite difference, assuming in the latter case that the bond order matrix is invariant for small changes in the geometry. In the HE treatment of open shell systems, however, this condition is not met and the derivatives calculated in this way are correspondingly inaccurate. The resulting errors cause serious problems in the DFP geometry program and in the location and identification of transition states. It becomes necessary to calculate the required derivatives by finite difference, using a complete SCF calculation to find the energy at each point. This is extremely time consuming and adds very greatly to the cost of the calculations.

There are two ways in which the problem can be circumvented.

The first is to use the Roothaan<sup>21</sup> restricted formalism for

open shell systems, with the generalized coupling operator (GCO) proposed by Hirao and Nakatsuji<sup>22</sup> and by Carbó et al.<sup>23</sup> We have written a MINDO/3 program, using this approach, and have used it to study a number of open shell systems.<sup>24</sup> Although the difficulty concerning invariance is avoided, the cost of the calculations unfortunately still remains excessive because of the much greater amount of computation involved compared with that in a standard restricted SCF treatment.

The second alternative is to use the Pople-Nesbet<sup>25</sup> unrestricted Hartree-Fock (UHF) formalism, and a corresponding version of MINDO/3 (UMINDO/3) is also now available.<sup>26</sup> This also avoids the problems concerning invariance, so derivatives can again be found very quickly and easily, while the computing time is just double that for a similar restricted treatment.<sup>27</sup> Use of UMINDO/3 suffers, however, from two important theoretical objections. First, such an unrestricted wave function is not an eigenfunction of  $S^2$  so it does not correspond properly to a real state of the molecule in question. Second, since use of the UHF formalism leads to an allowance for coulombic electron correlation and since electron correlation is taken into account in MINDO/3 via the parametrization, use of UMINDO/3 for an open shell system must lead to an overallowance for electron correlation and to energies that are consequently too negative (see ref 19).

The first problem did not raise any difficulties in the present case because the calculated expectation values of  $S^2$  indicated that the contamination by higher spin states was unimportant.

As regards the second, extensive tests<sup>24</sup> have shown that while the heats of formation calculated for radicals by UMINDO/3 are indeed systematically too negative, the errors do not vary greatly. Thus by making a fixed correction, one obtains values which agree with experiment about as well as do the MINDO/3 ones for closed shell molecules. One might therefore expect the errors due to excessive allowance for correlation to be more or less constant for a given potential surface. If so, UMINDO/3 should reproduce activation energies satisfactorily. As we shall see presently, this indeed seems to be the case. We have also found that the geometries given by the various open shell MINDO/3 treatments (i.e., UMINDO/3 and the GCO and HE versions of MINDO/3) for open shell species are almost identical, suggesting again that the overcompensation for correlation in UMINDO/3 does not lead to a distortion of the corresponding potential surface.

### Results and Discussion

Calculations were carried out with UMINDO/3 for the reactions of methyl radical with ethylene, acetylene, propene, and allene. In order to compare the performance of the three open shell MINDO/3 treatments, we also studied the reactions of methyl with ethylene and acetylene using the GCO and HE versions of MINDO/3.

**A. Reaction of Methyl with Ethylene.** The geometries, distributions of formal charge, and dipole moments calculated for the transition state (**1**), using UMINDO/3 and the GCO and HE versions, are shown in Table I. The calculated differences in energy between the reactants and the transition states (i.e., calculated activation energies) are listed in Table II.

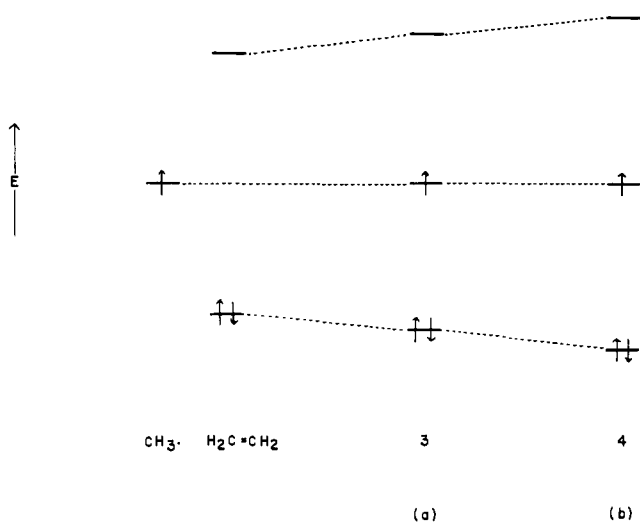
All three methods predict the approach of the methyl group to be very unsymmetrical (see **1**). There is no question of an intermediate  $\pi$  complex being formed. The transition state has  $C_v$  symmetry, the carbon atom and one hydrogen atom of the methyl group lying in the plane bisecting the two methylene groups.

The structure of the transition state is an interesting combination of reactant-like and product-like features. Thus the CCC bond angle ( $\phi$  in Table I) is close to the value in the product and the geometry of the methyl group is also nearer

**Table I.** Computed Properties of **1**

method	geometry <sup>a</sup>					formal atomic charges					dipole moment,	
	<i>r</i>	<i>R</i>	$\psi$	$\alpha$	$\beta$	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	H <sub>1</sub>	H <sub>2</sub>	H <sub>3</sub>	D
UHF	1.327	2.355	108.8	13.9	168.7	-0.021	0.002	-0.040	0.011	0.010	0.005	0.212
GCO	1.323	2.250	110.1	15.2	167.4	-0.015	0.006	-0.028	0.011	0.011	-0.002	0.111
H-E	1.318	2.300	108.8	14.1	168.5	-0.023	0.003	-0.064	0.012	0.008	0.007	0.114

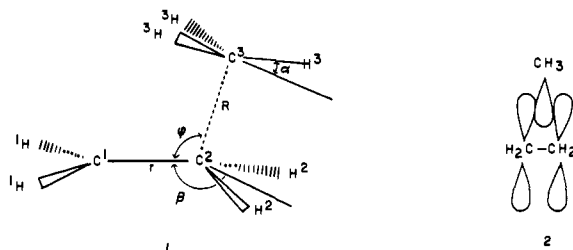
<sup>a</sup> Distances in ångströms, angles in degrees. For rotation, see **1**.



**Figure 1.** Change in orbital energies of methyl radical and ethylene on formation of (a) the transition state **3** (methyl planar) and (b) the transition state **4** (methyl pyramidal).

that in the product ( $\alpha$ ,  $19.5^\circ$ ) than in the reactant ( $\alpha$ ,  $0^\circ$ ). On the other hand, the forming CC bond is very long ( $\sim 2.3$  Å) and the rest of the transition state is definitely reactant-like. Thus the ethylenic CC bond length is only  $0.013$  Å greater than the value calculated for ethylene, and while the methylene group undergoing attack is tilted out of the plane defined by the rest of the ethylene moiety, the angle of tilt ( $11^\circ$ ) is much less than it is in the product ( $62^\circ$ ).

This result can in fact be very easily understood in terms of simple MO theory.<sup>28</sup>  $\sigma$ -Type overlap of the singly occupied 2p AO of methyl radical with one of the terminal 2p AO's contributing to the ethylenic  $\pi$  bond gives rise to a system isoconjugate with the allyl radical (Figure 1a). The result is a decrease in energy of the three electrons occupying the resulting three-center MO's. This interaction leads, as in the allyl radical, to three MO's, one strongly bonding, one nonbonding, and one antibonding. If the AO of the methyl radical overlapped symmetrically with both 2p AO's forming the ethylenic  $\pi$  bond, the resulting system would be isoconjugate with the cyclopropenyl radical in which two of the three  $\pi$  MO's are antibonding. The unpaired electron in cyclopropenyl radical consequently occupies an antibonding MO, in contrast to allyl radical where the singly occupied MO is nonbonding. For this reason the cyclopropenyl radical is antiaromatic;<sup>29</sup> likewise the symmetrical  $\pi$  complex structure (**2**) for the methyl-eth-

**Table II.** Calculated and Observed Activation Energies

reaction	activation energy, kcal/mol			
	obsd	UHF	GCO	H-E
CH <sub>3</sub> + H <sub>2</sub> C=CH <sub>2</sub>	7.2-7.9 <sup>a</sup>	7.9	8.6	13.4
CH <sub>3</sub> + CH≡CH	7.7 <sup>b</sup>	6.8	7.6	11.2
CH <sub>3</sub> + H <sub>2</sub> C=CHCH <sub>3</sub>	7.4 <sup>c</sup>	7.4		
		11.7		
CH <sub>3</sub> + H <sub>2</sub> C=C=CH <sub>2</sub>	8.1 <sup>d</sup>	6.9		
		11.7		

<sup>a</sup> Reference 4. <sup>b</sup> J. A. Garcia-Dominguez and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 940 (1962). <sup>c</sup> R. J. Cvetzanovic and R. S. Irwin, *J. Chem. Phys.*, **46**, 1694 (1967). <sup>d</sup> R. R. Getty, J. A. Kerr, and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 979 (1967).

ylene adduct is less stable than the unsymmetrical one **1**. This argument was indeed used in a very early presentation of the  $\pi$  complex theory to explain the difference between electrophilic addition to olefins, and analogous radical or nucleophilic additions.<sup>29</sup> The antiaromaticity of cyclopropenyl radical has been established by experiment and is also indicated by MINDO/3; see Bischoff.<sup>30</sup>

Consider now the unsymmetrical transition state **1**. Distortion of the methyl group into a tetrahedral geometry converts the singly occupied AO from a pure p AO to an sp<sup>3</sup> hybrid. The latter will overlap much more efficiently with the adjacent ethylenic 2p AO (**4**) so (Figure 1b) the interaction



energy is correspondingly increased and the transition state is correspondingly stabilized. However, little would be gained by an analogous rehybridization of the central carbon atom in **3** because (see **5**) the resulting increase in  $\sigma$ -type overlap with the methyl AO would be offset by a corresponding decrease in overlap with the 2p AO of the other ethylenic carbon atom. As a result the methyl group adopts a product-like configuration in the transition state while the ethylenic moiety remains reactant-like. This accounts for the apparent conflict noted above between evidence<sup>8</sup> from secondary isotope effects, which indicates the ethylene moiety to be reactant-like in the transition state, and kinetic evidence,<sup>9</sup> which suggests that the CH<sub>3</sub>-C bond has been largely formed. We would predict a large secondary isotope effect of deuterium in the methyl, CH<sub>3</sub>, reacting more rapidly than CD<sub>3</sub>. Our description of the transition state is also supported by the calculated (UMIN-

Table III. Computed Properties of 6

method	geometry <sup>a</sup>						formal atomic charges						dipole moment, D
	r	R	$\psi$	$\alpha$	$\beta$	$\gamma$	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	H <sub>1</sub>	H <sub>2</sub>	H <sub>3</sub>	
UHF	1.203	2.352	114.3	14.0	15.9	10.3	-0.106	-0.091	-0.034	0.110	0.111	0.004	0.189
GCO	1.203	2.300	115.4	14.6	16.5	10.4	-0.104	-0.090	-0.024	0.110	0.112	-0.001	0.150
H-E	1.201	2.252	114.3	14.6	16.1	10.4	-0.109	-0.061	0.056	0.113	0.106	0.003	0.100

<sup>a</sup> Distances in ångströms, angles in degrees. For notation, see 6.

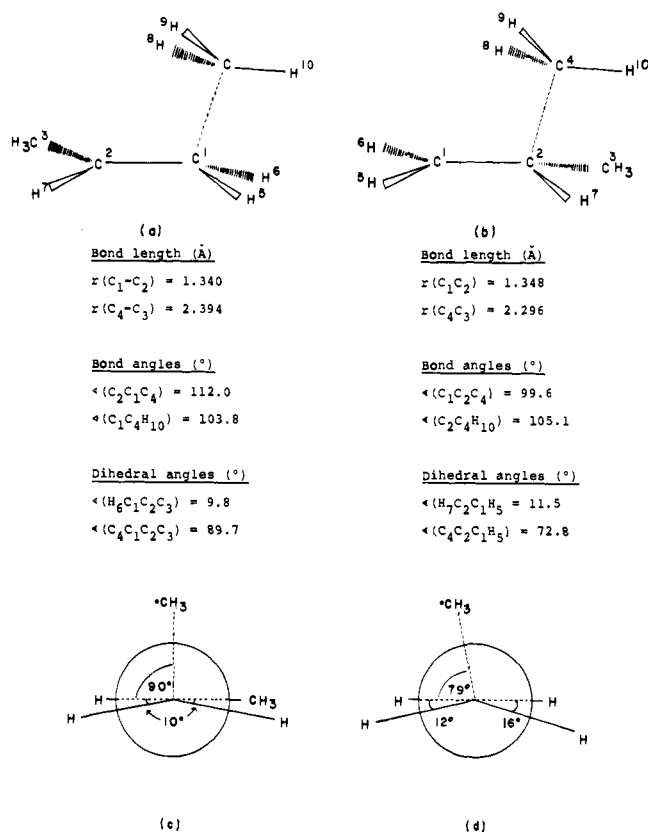


Figure 2. Calculated bond lengths ( $ij$ ) (in Å), bond angles ( $ijk$ ), and dihedral angles ( $ijkl$ ) for (a) 8 and (b) 9. Newman projections along the C=C bond for (a) 8 and (b) 9.

DO/3) distribution of unpaired electron, shown in Figure 2a, and by the very small formal charges at the individual atoms and the correspondingly small dipole moment (Table I).

The activation energies calculated by the UMINDO/3 and GCO procedures agree well with each other and with the experimental value (Table II). The EH value is appreciably greater, though still within the limits of error of MINDO/3. UMINDO/3 seems the most satisfactory of the three procedures in this connection, a pleasing conclusion since it also requires the least amount of computation.

We also studied the energy of the product ( $n$ -Pr $\cdot$ ) as a function of the angle of rotation of the (planar) terminal methylene group about the CH<sub>2</sub>-CH<sub>2</sub> bond. Two stable conformations were found, one with the C-CH<sub>3</sub> bond lying in the nodal plane of the singly occupied AO, the other with it orthogonal to that plane (Figures 3a and 3b). The former was found to be lower in energy by 0.4 kcal/mol. These conclusions agree very nicely with ESR studies of  $n$ -propyl radical by Fessenden<sup>31</sup> and by Krussic and Kochi.<sup>32</sup>

**B. Reaction of Methyl with Acetylene.** Table III summarizes the results of calculations by the three open shell MINDO/3 procedures for the transition state for addition of methyl radical to acetylene. Here again all three methods lead to similar results.

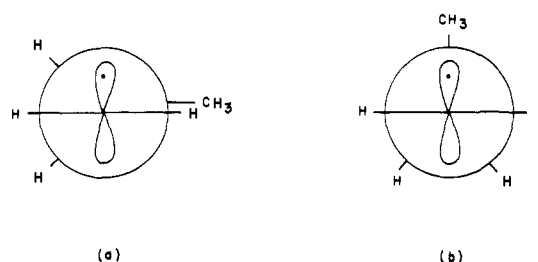
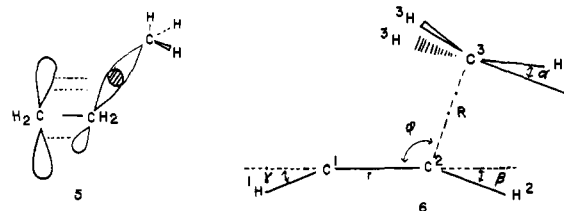


Figure 3. Stable conformations of the  $n$ -propyl radical.

As in the case of the reaction of methyl with ethylene, the transition state (6) has an ambiguous structure, partly reac-



tant-like and partly product-like. Thus the geometry of the methyl group is almost identical with that in the methyl-ethylene transition state (cf. Tables I, III) and the value of the CCC bond angle is close to that in the product,  $\alpha$ -methylvinyl (7). On the other hand the forming bond is again still very long

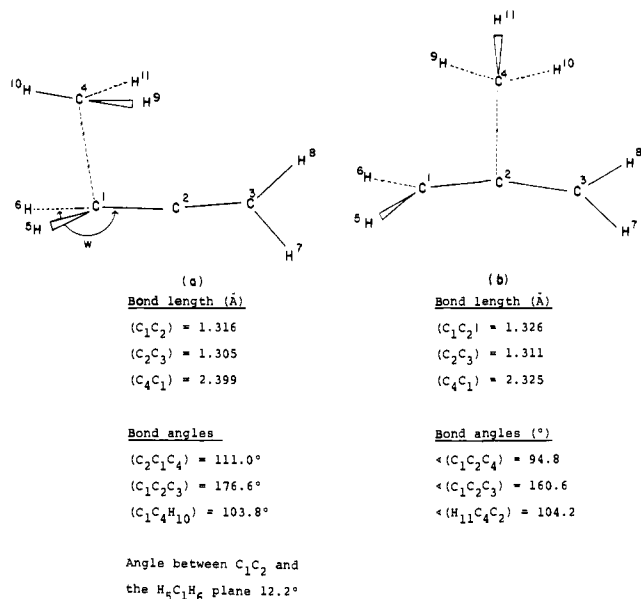


( $\sim 2.3$  Å), the acetylenic CC bond is only 0.007 Å longer than the value calculated for acetylene, and the angles of tilt to the acetylenic hydrogen atoms ( $\beta$  and  $\gamma$  in Table III) are nearer to the values in acetylene ( $0^\circ$ ) than in the product ( $\beta = 36^\circ$ ,  $\gamma = 66^\circ$ ). The situation here is of course similar to that in the methyl-ethylene transition state, both transition states being isoconjugate with the allyl radical. Note that *both* acetylenic hydrogen atoms are tilted to comparable degrees in the transition state. This of course is due to the fact that the corresponding HCC bond angles both change during the reaction. In the reactions of methyl radical with ethylene, the terminal methylene group remains almost unchanged in geometry.

Here again the activation energies calculated by UMINDO/3 and GCO agree very well with experiment (Table II) while the HE value is again greater by ca 4 kcal/mol. The distribution of unpaired electron in the transition state (Figure 2b) is similar to that in the methyl-ethylene transition state.

In view of the close correspondence between the results given by UMINDO/3 and the two other open shell treatments (GCO, HE) and in view of the much lower cost of the UMINDO/3 calculations, the remaining reactions were studied only with UMINDO/3.

**C. Reaction of Methyl with Propene.** The reaction of methyl radical with propene is of interest because it provides the simplest test of the ability of MINDO/3 to predict the position



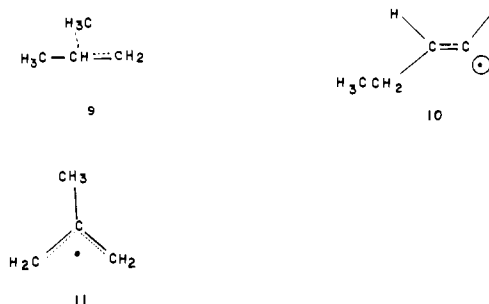
**Figure 4.** Calculated bonds lengths (*ij*) (in Å) and bond angles in the transition states for reaction of methyl radical with allene to form (a) **10** and (b) **11**.

of attack in the addition of radicals to unsymmetrical olefins. The calculated (UMINDO/3) structures of the transition states for 1 and 2 addition to propene (**8** and **9**) are shown in Figure 2 and the corresponding calculated activation energies are shown in Table II.

It will be seen that MINDO/3 correctly predicts the preferred mode of attack to be that indicated in **8**, leading to 2-butyl radical. The calculated activation energy is very similar to that for addition to ethylene, again in agreement with experiment (Table II). The difference in rate between the two modes of addition is not known experimentally. Our estimated value for the difference between the two activation energies (4.3 kcal/mol) is consistent with the greatly reduced reactivity of olefins lacking a free terminal methylene group, indicated by studies of polymerization and copolymerization.<sup>33</sup>

The structure (Figure 4a) of the transition state for the preferred reaction (**7**) is very similar to that for the methyl-ethylene addition (Figure 1). The structure (Figure 4b) of the other transition state (**9**), however, differs significantly in two respects. First, the direction of approach of the methyl group is different, the angle C<sub>1</sub>C<sub>2</sub>C<sub>4</sub> in Figure 4b being much smaller (99.6°) than the corresponding angles in **1** (109.8°) or **8** (112.0°) and the forming CC bond no longer lying in a plane orthogonal to the terminal methylene group (see Figure 4c). Second, the central CHCH<sub>3</sub> group is not only tilted out of plane of the terminal methylene but also rotated (Figures 4c). These distortions are clearly due to repulsions between the two methyl groups, which in turn are presumably responsible for the difference in energy between the two transition states. A vestigial methyl-methyl interaction in **8** may be reflected by the fact that the CCC bond angle in **1** (109.8°) is slightly smaller than the corresponding angle in **7** (112.0°).

**D. Addition of Methyl Radical to Allene.** The addition of methyl radical to allene provides another interesting test of UMINDO/3 because this is one of the few such reactions that leads to the *less* stable of the two possible products. In the case of propene, for example, terminal addition of a radical X• gives a secondary alkyl radical (XCH<sub>2</sub>CHCH<sub>3</sub>) which is more stable than the primary radical (CH<sub>2</sub>CHXCH<sub>3</sub>) which would be formed by central addition. Addition to allene, however, also takes place most readily at the terminal carbon atom to form 1-ethylvinyl radical (**10**), although this is of course less stable



than the 2-methylallyl radical (**11**) that would be formed by central addition.

Table II shows the activation energies calculated by UMINDO/3 for the two modes of addition to allene. It will be seen that the value for terminal addition is the lesser, in agreement with experiment, and the calculated and observed values for terminal addition also agree well with one another.

The greater ease of terminal addition is due to the fact that a geometrical rearrangement has to occur during central addition. In allene or **9**, the methylene groups lie (or can lie) in orthogonal planes whereas in **10** they are coplanar. The coplanar form of allene is much higher in energy than the orthogonal one, the difference between them being equal to the barrier to rotation which is calculated<sup>15b</sup> and observed<sup>34</sup> to be ca. 47 kcal/mol. Until the addition of methyl radical to the central carbon atom has progressed to a major extent, rotation of the methylene group into coplanarity will then remain unfavorable. However, in each of the three cases so far considered, bonding of the methyl group to the substrate has occurred only to a very small extent in the transition state. It is therefore only to be expected that the methylene groups remain orthogonal in the transition state for addition of methyl radical to allene. Consequently none of the resonance effects present in the product are available in the transition state. The transition state for terminal addition is therefore lower in energy than that for central addition, partly because of the hyperconjugative effect of methyl and partly because of a steric interaction between the approaching methyl and one of the terminal allene hydrogen atoms, analogous to the similar interaction that is apparently responsible for the terminal addition to propene (see above).

The geometries of the transition states are shown in Figure 3.

## Conclusions

The work reported here seems to be the first detailed study to be reported of a series of free-radical reactions, using MINDO/3. The results suggest that MINDO/3 is as applicable to such processes as to those involving only closed shell species, a gratifying conclusion in view of the practical importance of free-radical reactions. The geometries calculated for the transition states account for apparent conflicts in the experimental evidence and also indicate the importance of steric effects in determining the course the reactions take. Thus the preferential terminal attack on propene seems to be due mainly to steric effects. The unrestricted version of MINDO/3 (UMINDO/3) seems to give results at least as good as the alternative procedures for treating open shell systems, a satisfactory conclusion since UMINDO/3 also requires much less computing time.

The success of these calculations for the reactions of methyl radicals with simple unsaturated hydrocarbons suggests that useful information would be provided by an analogous treatment of other radical addition reactions.

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## Calculation of Phosphororganic Compounds by MINDO/3. 1. Parametrization of the P-C Bond

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**Abstract:** The original parameters  $\alpha_{XY}$  and  $B_{XY}$  for the core repulsion and the resonance integrals in MINDO/3 were found to be incorrect in case of the P-C bonding. New parameters were determined based on true experimental data.

The semiempirical method MINDO/3 was developed by Dewar et al.<sup>1</sup> Calculations in a wide field of chemical compounds showed good results. It is our aim to apply MINDO/3 systematically for phosphororganic compounds which has been done for only a small number of molecules by Dewar et al.<sup>2</sup> The parameters  $\alpha_{XY}$  for the core repulsion and  $B_{XY}$  for the resonance integrals were only given for P-C, P-P, and P-H bonding. When we recalculated the molecules reported by Dewar et al.<sup>2</sup> we could not reproduce the same results in the case of P-C bonding; a complete optimization of all independent geometrical parameters gave much lower values for the heat of formation. This is shown in Table I. Therefore we found it necessary to determine new values for  $\alpha_{XY}$  and  $B_{XY}$  for P-C bonding. Furthermore, we found the experimental values used by Dewar et al. not very reliable. The only true experimental value used for the parametrization was that for trimethylphosphine ( $M_3$ ), whereas the other values of dimethylphosphine ( $M_2$ ), methylphosphine ( $M_1$ ), and the ethylphosphines ( $E_1$  and  $E_2$ ) were determined by calculations using an increment method based upon the values for  $M_3$  and  $PH_3$ .<sup>3</sup> The reported experimental value for the heat of formation of

triethylphosphine ( $E_3$ )<sup>4</sup> shows the values for the ethylphosphines to be in error.

We based our parametrization only on experimental values, that is  $M_3$ ,  $E_3$ , and the value for tri-*n*-butylphosphine.<sup>4</sup> The results are shown in Table I. The new values for  $\alpha_{XY}$  and  $B_{XY}$  are 0.8700 and 0.5000, respectively. Table II shows the calculated ionization potentials, that is the negative eigenvalue of the HOMO, in comparison to experimental values and Dewar's results. In Table III the geometrical data are presented, together with experimental values. In all cases, the deviation from Dewar's results is not strong and the agreement with experimental results is good.

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**Note Added by M. J. S. Dewar and G. P. Ford:** We have checked the calculations for phosphorus compounds and confirmed that the results listed in ref 2 do not follow from the parameters listed in ref 1. We have also repeated calculations