

## A Theoretical Model for the Baeyer-Villiger Rearrangement

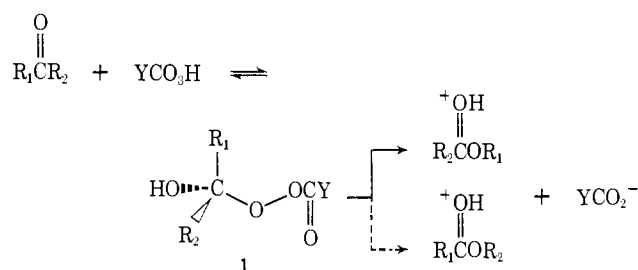
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**Abstract:** Nonempirical SCF-MO calculations and an all-valence-electron semiempirical SCF-MO treatment with complete neglect of differential overlap (CNDO/2) have been used to trace a methyl group migration from carbon to oxygen:  $\text{CH}_3\text{CH}(\text{OH})-\text{OX} \rightarrow \text{HC}(=\text{O}^+\text{OH})\text{OCH}_3 + \text{X}^-$ . This migration models the rate-determining rearrangement step in the Baeyer-Villiger reaction, and the theoretical predictions are in good agreement with the experimental results, where available. The calculations suggest that an upper limit for the position of the transition state is 75% along the reaction coordinate. Migration to cationic oxygen appears to be ruled out, and an earlier transition state is observed with  $\text{X}^- = \text{F}^-$  than with  $\text{X}^- = \text{H}^-$  as the leaving group. The optimized transition state geometry indicates little reorganization in the migrating group as well as considerable carbonyl formation, results which concur with the small  $\alpha$  and relatively large  $\beta$  secondary deuterium isotope effects measured for this rearrangement.

The Baeyer-Villiger reaction<sup>1</sup> has been shown to occur by a two-step mechanism (Scheme I) in which

Scheme I



Criegee's structure **1**<sup>2a</sup> is commonly accepted as a transient intermediate. While **1** has never been observed in the course of a rearrangement reaction, analogous structures are known for addition of peroxyacetic acid to aldehydes.<sup>2b</sup> A large body of experimental evidence supports assignment of structure **1** as the intermediate.<sup>1,2</sup> In a number of instances, the migration step has been shown to be rate limiting.<sup>3</sup>

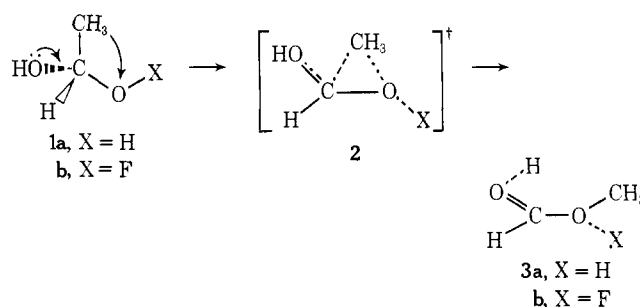
In this paper we direct our attention to the hypersurface connecting the tetrahedral intermediate with the product. Some inferences on this step have been made on the basis of experimental data. Migratory aptitude trends indicate that the bulk of a group,<sup>4</sup> its ability to support positive charge,<sup>5-7</sup> and the size and

reactivity of the peracid,<sup>4,8</sup> involved in the oxidation, influence the energy of the rearrangement transition state and hence its position along the reaction coordinate.<sup>9</sup>

There are, however, certain aspects of the migration step, which cannot be delineated from these experimental results alone: the position of the transition state has been called "relatively early"<sup>3a</sup> or "relatively late" depending on the reaction conditions used or the comparison being made.<sup>4</sup> Effects of the leaving group on the transition state for migration have been observed,<sup>4,7,8</sup> yet it is not clear whether these effects are exerted in an activated complex formed synchronously from the tetrahedral intermediate **1**, or whether **1** first forms an intimate ion pair, which then undergoes rearrangement.<sup>10</sup>

We report a theoretical investigation of a model reaction (Scheme II), simulating the migration step alone.

Scheme II



In this work, we present the energy profiles, obtained from *ab initio* and CNDO/2 calculations, for methyl migration from carbon to oxygen, with H as the non-migrating group and  $\text{H}^-$  or  $\text{F}^-$  replacing the carboxylate leaving group  $\text{YCO}_2^-$ . Conclusions are drawn about the upper limit for the position of the transition state along the migration coordinate, and the effect of the leaving group on this position is noted. Synchronous *vs.* two-step migration is discussed in terms of the energy dependence of transient species on the extent

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(2) (a) R. Criegee, *Justus Liebigs Ann. Chem.*, **560**, 127 (1948); (b) B. Phillips, *J. Amer. Chem. Soc.*, **79**, 5982 (1957); (c) W. von E. Doering and E. Dorfman, *ibid.*, **75**, 5595 (1953); for another intermediate see (d) H. Kwart, P. S. Starcher, and S. W. Tinsley, *Chem. Commun.*, 335 (1967).

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(4) M. A. Winnik and V. Stoute, *Can. J. Chem.*, **51**, 2788 (1973).

(5) W. von E. Doering and L. Speers, *J. Amer. Chem. Soc.*, **72**, 5515 (1950).

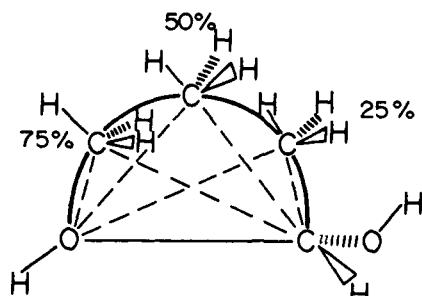
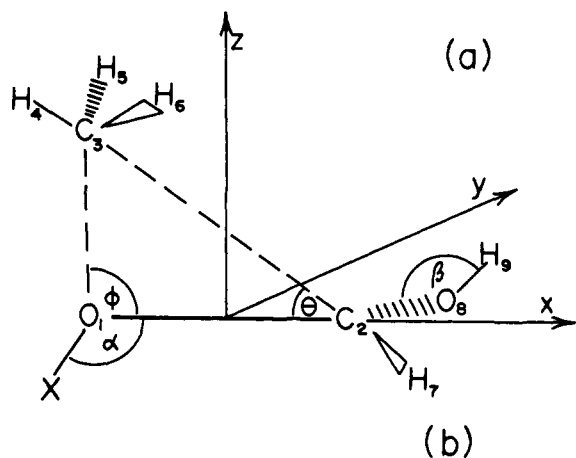
(6) Y. Yukawa and T. Yokoyama, *Mem. Inst. Sci. Ind. Res. Osaka Univ.*, **13**, 171 (1956); *Chem. Abstr. Jap.*, **51**, 2633h (1957).

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(8) R. W. White and W. D. Emmons, *Tetrahedron*, **17**, 31 (1962).

(9) G. S. Hammond, *J. Amer. Chem. Soc.*, **77**, 334 (1955).

(10) This point is discussed in ref 1c, pp 581, 582.



**Figure 1.** (a) The generalized system in a right-handed Cartesian framework. The numbering is that used in the text. (b) Schematic representation of methyl migration from carbon to oxygen. The heavy line depicts the path of methyl movement.

of bond breaking between the migration terminus and the leaving group. In addition to the main calculations, population analyses of the transient species along the reaction coordinate were made, and these are interpreted semiquantitatively in terms of electron flow through the system during  $\text{CH}_3$  migration. Finally, the possible implications of the optimized transition state geometry are outlined.

#### Method of Calculation

(i) **Computational Details.** All computations were carried out on an IBM 370/165 computer. The molecular integrals for the *ab initio* SCF-MO calculations were obtained by IBMOL (VERSION IV),<sup>11</sup> employing atomic orbitals built up from primitive Gaussian-type functions (GTF). The basis set chosen as recommended by Klessinger,<sup>12</sup> was made up of contracted basis functions: for carbon and oxygen atoms, ( $8^s, 3^p$ ) was contracted to [ $2^s, 1^p$ ], and for hydrogen, ( $3^s$ ) to [ $1^s$ ]. The SCF calculations involved the use of the POLYATOM system.<sup>13</sup>

The semiempirical SCF-MO wave functions were computed with the CNDO/2 method developed by Pople and coworkers.<sup>14,15</sup> The AO parameters used for CNDO/2 were those originally reported<sup>14,15</sup> by these authors.

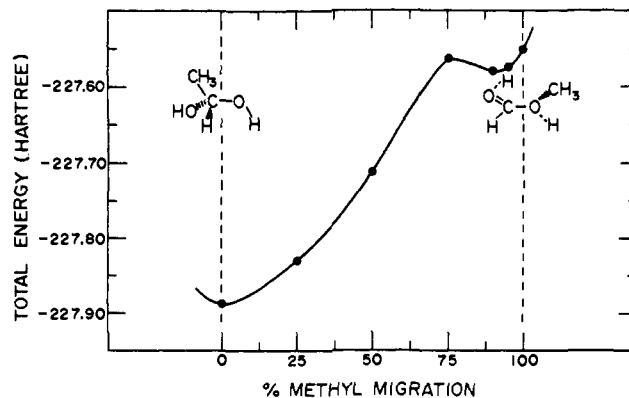
(11) A. Veillard, "Ibmol: Computation of Wave Function for Molecules of General Geometry, Version IV," IBM Research Laboratory, San Jose, Calif.

(12) M. Klessinger, *Theor. Chim. Acta*, **15**, 353 (1969).

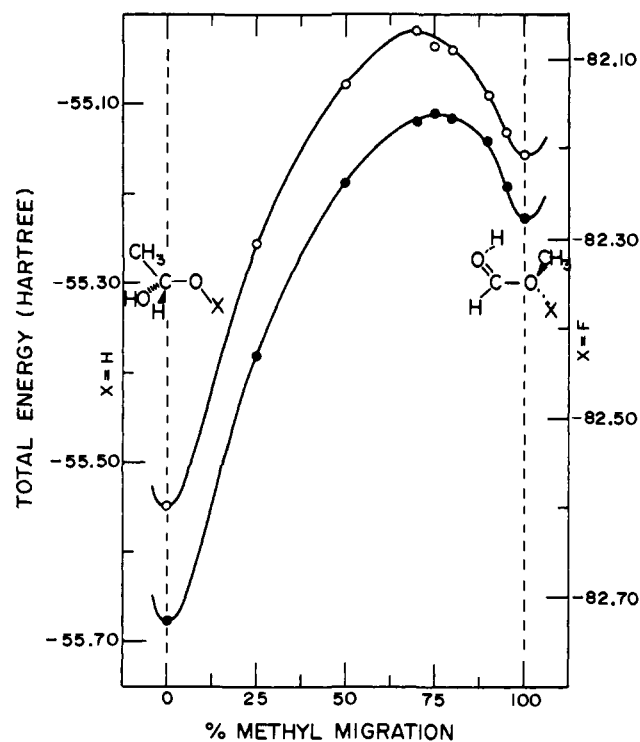
(13) I. G. Csizmadia, *et al.*, "The POLYATOM System," Quantum Chemistry Programme Exchange, Catalogue No. 47A.

(14) J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, **43**, 5129 (1965).

(15) J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **43**, 5136 (1965); **44**, 3289 (1966).



**Figure 2.** Variation of total energy (*ab initio*) with per cent methyl migration for X = H.



**Figure 3.** Variation of total energy (CNDO/2) with per cent methyl migration for X = H (●) and X = F (○).

(ii) **Geometry.** Generation of a complete potential energy surface for the rearrangement in Scheme II would require methodically minimizing the total energy of the system (Figure 1a) with respect to all its independent internal coordinates. The size of the system makes this unfeasible. Instead, investigation centered around the migration cross section (Figure 1b), assumed to be close to the reaction coordinate passing through the equilibrium geometry. Seven (*ab initio*) and two sets of nine (CNDO/2) points were chosen to form a path representing the methyl migration from carbon to oxygen. The energies of these points are listed in Table I and plotted in Figures 2 and 3. The bond lengths and bond angles thought to be most affected by the movement of the methyl group were varied synchronously. Others, not directly involved, were kept constant. The very basic but reasonable assumption was made that the beginning (1a or 1b) and end (3a or 3b) of methyl migration represent two limits between which the

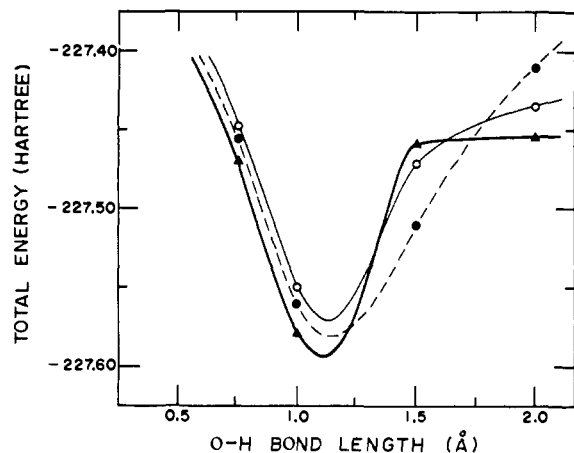


Figure 4. Variation of total energy (*ab initio*) with O-X (X = H) bond length for points 75 (---●---), 90 (---▲---), and 100% (---○---) along the migration coordinate.

Table I. Computed Total Energies for the Reactant, Transient Species, and Product of the Rearrangement in Scheme II

% methyl migration	Total energy, hartrees		
	X = H <i>Ab initio</i>	X = H CNDO/2	X = F CNDO/2
0	-227.8919	-55.6772	-82.6016
25	-227.8311	-55.3817	-82.3087
50	-227.7137	-55.1880	-82.1258
70		-55.1192	-82.0693
75	-227.5678	-55.1136	-82.0860
80		-55.1151	-82.0889
90	-227.5778	-55.1406	-82.1430
95	-227.5727	-55.1931	-82.1819
100	-227.5493	-55.2240	-82.2047

change in certain parameters would be linear. For example, in formation of the carbonyl double bond, the development of planarity for  $H_7C_2O_1O_8$  and the tightening of the bond between the migration origin and terminus must all occur at the same rate as the shifting of the methyl group, in order to maintain a balanced electron flow through the system.

Values for the geometrical parameters of **1a(b)** and **3a(b)** are listed in Table II. The bond lengths and bond angles for **1a(b)**, with the exception of the O-X bond, were taken from standard tables.<sup>16</sup> The values used for the O-X (X = H, F) bond were larger than those quoted<sup>17,18</sup> for ordinary single bonds of these types. Basically the same geometry as that obtained from the microwave spectroscopic study<sup>19</sup> of methyl formate was retained for **3a(b)**. The methyl group, however, was considered to be rotated 90° out of the plane  $H_7C_2O_1O_8$ , keeping it anti-periplanar to the group X.

For the configurations, intermediate between **1a** and **3a** (or **1b** and **3b**) along the reaction coordinate, values between the limits in Table II were selected for most of the geometrical parameters. Values for  $\beta$ ,  $\gamma$ ,  $\alpha$ , HCH, and  $r(O_8-H_9)$  were kept constant throughout.  $r(O-X)$  (X = H, F) was kept constant while the other param-

(16) "Table of Interatomic Distances," *Chem. Soc., Spec. Publ.*, No. 11 (1958); No. 18 (1965).

(17) Reference 16 lists the values of the O-H bond in  $H_2O$  and  $CH_3OH$  as 0.957 and  $0.960 \pm 0.015$  Å, respectively.

(18) (a) A. P. Hilton Jr., A. W. Jache, J. B. Beal, Jr., W. D. Henderson, and R. J. Robinson, *J. Chem. Phys.*, **34**, 1137 (1961); (b) L. Pierce and R. Jackson, *ibid.*, **35**, 2240 (1961).

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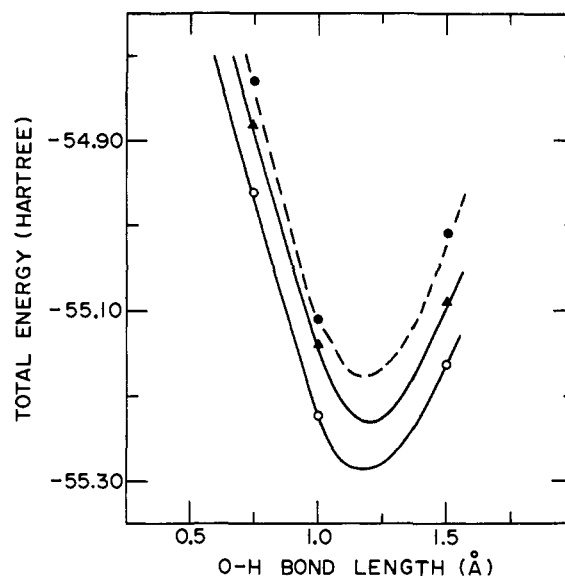


Figure 5. Variation of total energy (CNDO/2) with O-X (X = H) bond length for points 75 (---●---), 90 (---▲---), and 100% (---○---) along the migration coordinate.

Table II. Molecular Geometries for the Reactant, Product, and Transition State of the Rearrangement in Scheme II

Parameters <sup>a</sup>	Value <sup>b</sup>		Transition State
	1a(b)	3a(b)	
O <sub>1</sub> -C <sub>2</sub>	1.43	1.33	1.34
O <sub>1</sub> -C <sub>3</sub>	2.43 <sup>c</sup>	1.44	1.91
C <sub>2</sub> -C <sub>3</sub>	1.54	2.34	2.39
C <sub>2</sub> -C <sub>7</sub>	1.07	1.10	1.125
C <sub>2</sub> -O <sub>8</sub>	1.43	1.20	1.27
$\gamma(C_3-H_4=C_3-C_5=C_3-H_6)$	1.10	1.10	1.12
O <sub>8</sub> -H <sub>9</sub>	0.96	0.96	1.00
O-X, X = H	1.00 <sup>d</sup>	1.00 <sup>d</sup>	1.00
X = F	1.47 <sup>e</sup>	1.47 <sup>e</sup>	
$\theta$	109.5 <sup>f</sup>	35.87 <sup>c</sup>	95.42
$\phi$	36.75 <sup>c</sup>	115	52.7
$\angle HCH$ ( $\angle H_4C_3H_5 = \angle H_4C_3H_6 = \angle H_5C_3H_6$ )	110	110	112
$\beta$	110	110	110
$\alpha$	110	110	110

<sup>a</sup> Cf. Figure 1 for numbering of atoms. <sup>b</sup> Values for **1a(b)** and **3a(b)** were taken from ref 16 and ref 19, respectively, unless otherwise indicated. The transition state values were systematically optimized by CNDO/2. The O-X (X = H) bond was optimized by *ab initio* as well. Bond lengths in ångströms; angles in degrees.

<sup>c</sup> Application of the law of cosines for a triangle (formed by O<sub>1</sub>C<sub>2</sub>C<sub>3</sub>): viz.  $a^2 = b^2 + c^2 - 2bc \cos w$ , where all parameters, except one of the bond lengths  $a$ ,  $b$ ,  $c$  or the angle  $w$ , are known. <sup>d</sup> Slightly loosened bond; cf. with O-H bond length in  $H_2O$  and alcohols (ref 17). <sup>e</sup> Longer bond than the O-F bond in  $OF_2$  (ref 18). <sup>f</sup> Theoretical tetrahedral angle. A distorted tetrahedral geometry for **1a(b)** is more realistic, but small changes in this angle will not change the trends observed.

eters were varied and then, in a subsequent step, the effect of this bond length (X = H) on energy was checked for configurations corresponding to 75, 90, and 100% migration (Figures 4 and 5). The only other parameters not varied linearly were  $r(C_2-C_3)$  and  $r(O_1-C_3)$ . These were always given values dictated (because of geometrical considerations) by those of  $\theta$ ,  $\phi$ , and  $r(C_2-O_1)$  selected.

At this point, it is worthwhile to elaborate somewhat on the experimental results, incorporated into the theoretical model to make the geometries assigned best

approximate those of the transient species along the reaction coordinate. In the Baeyer–Villiger oxidation, the migrating group is believed to move with its pair of bonding electrons. In this case, then, the methyl group can be visualized (Figure 1b) as moving in a migration arc. The original electron pair of the  $\text{CH}_3\text{—C}$  bond is taken as an electron density vector resolved along two changing nonorthogonal axes, which always lead to the migration origin (carbon) and terminus (oxygen).<sup>20</sup> The reaction is known to proceed with retention of the configuration of the migrating group.<sup>21</sup> This dictates that the carbon center of the methyl group with its three full bonds and two partial bonds be given  $C_s$  symmetry.<sup>22,23</sup> The ternary axis of the  $\text{H}_4\text{H}_5\text{H}_6\text{C}_3$  pyramid was always taken as cutting the  $\text{C}_2\text{—O}_1$  bond at right angles.<sup>24</sup>

In this system, it was impossible to estimate the values of some input parameters (*viz.* angles of rotation of bonds out of chosen reference planes) for the standard computer programs, which calculate atomic coordinates. They were obtained, therefore, by elementary vector analysis.

## Results and Discussion

**Position of the Transition State.** Figure 2 shows the energy profile along the migration path, predicted by the *ab initio* calculations, for the rearrangement in Scheme II ( $\text{X} = \text{H}$ ). In all the configurations used to obtain the points on this plot, the value of the  $\text{O—X}$  bond was taken as 1.0 Å. The energy profiles obtained from CNDO/2 calculations for the same rearrangement where  $\text{X} = \text{H}$  and  $\text{X} = \text{F}$  are shown in Figure 3. The  $\text{O—H}$  bond was again taken as 1.0 Å and the  $\text{O—F}$  bond as 1.47 Å for all the species. The computed total energy values are summarized in Table I.

There are some discrepancies between the *ab initio* and CNDO/2 profiles for  $\text{X} = \text{H}$ , but they both predict a maximum (in the case of the former, a local maximum) at a position 75% along the coordinate representing migration of methyl from carbon to oxygen. The *ab initio* results further indicate an increase in energy after the 90% position so that the energy of **3a**, which denotes the termination of migration, is higher than that of the species, in which only 75% of the methyl movement has been completed. This last detail will be discussed after the results of the  $\text{O—H}$  bond-length variations are outlined in the following section.

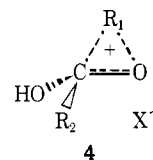
In view of the fact that *ab initio* and CNDO/2 methods give substantially the same result for  $\text{X} = \text{H}$  (*viz.* a migration transition state at the 75% position), it was thought sufficient, for economic reasons, to use the CNDO/2 method for a comparison of leaving groups where  $\text{X} = \text{H}$  and  $\text{X} = \text{F}$ . One fact is immediately clear on examination of the two energy profiles in Figure 3: the maximum in the profile for  $\text{X} = \text{H}$  occurs later in the course of the reaction. This agrees

with the conclusion, based on experiments in solution, that the reactivity of the peracid used (and hence the stability of the leaving group  $\text{YCOO}^-$  in Scheme I) influences the position of the transition state. The better leaving group promotes the earlier transition state.<sup>9</sup> Experimental results<sup>4,8</sup> also indicate that the size of the peracid is important, because the leaving group interacts sterically with the nonmigrating group.

$\text{F}^-$  and  $\text{H}^-$  are approximately isosteric so there should be little difference in their interaction with the nonmigrating group ( $\text{H}_7$ ) here. There are electronic differences between them, however, and the theoretical calculations parallel the experimental results in predicting what effect these differences have on the positions of the transition states. They add a further refinement: they designate a limit along the migration coordinate beyond which the transition state for a Baeyer–Villiger reaction should not occur.

From electronic considerations alone,  $\text{H}^-$  should be a worse leaving group than any carboxylate anion  $\text{YCO}_2^-$ . Based on the properties of the leaving group alone, the position of the transition state for the reaction where  $\text{X} = \text{H}$  (75%) should constitute an upper limit for the “lateness” of the transition state in this kind of rearrangement. Alterations in both the migrating and nonmigrating groups, however, could modify this limit. An increase in the migratory aptitude of the former would decrease the energy of the transition state,<sup>4</sup> making it more reactant-like.<sup>9</sup> On the other hand, an increase in the size of the nonmigrating group would increase the energy of the transition state and make it more product-like. Furthermore, ketone substrates undergoing the Baeyer–Villiger reaction often involve larger nonmigrating groups than  $\text{H}$  and better migrating groups than methyl. These changes work in opposite directions and would tend to cancel each other.

**Synchronous vs. Two-Step Rearrangement.** Evidence that the steric and electronic natures of the leaving group both affect the energy of the transition state is generally interpreted in terms of  $\text{O—X}$  bond cleavage synchronous with migration of a group from carbon to oxygen. Such evidence, however, is not inconsistent with migration taking place in an intimate ion pair (**4**).



Here the leaving group should still be close enough to interact sterically with the nonmigrating group ( $\text{R}_2$ ). A change in mechanism with peroxyacid structure would then explain the variations observed in the amount of positive charge delocalized onto the migrating group  $\text{R}_1$ . Changing from a concerted mechanism to one involving **4** would cause the migrating group to look more positive in the transition state. Thus, experimental data do not rule out the possibility of limiting cases in which two-step rearrangement can occur. The  $\text{O—X}$  ( $\text{X} = \text{H}$ ) bond length was varied by *ab initio* and CNDO/2 methods for certain configurations. These variations are presented in Figures 4 and 5 as

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(23) W. Th. A. M. Van der Lugt and P. Ros, *Chem. Phys. Lett.*, **4**, 389 (1969).

(24) A. Gamba, G. Morosi, and M. Simonetta, *Chem. Phys. Lett.*, **3**, 21 (1969).

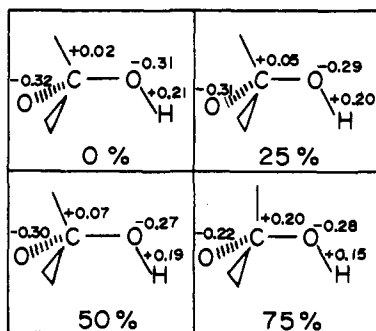


Figure 6. Net charges on the atoms directly involved in migration for configurations representing 0 to 75% migration.

projections perpendicular to the migration path in the 75, 90, and 100% regions. Both *ab initio* and CNDO/2 calculations indicate that the optimum bond length for all the configurations examined is 1.0 Å. If one defines the reaction path as the path of least resistance (from reactants to products) through the potential energy surface, then migration to cationic oxygen is ruled out as a feasible representative. Completely breaking the O-X bond first would raise the energy of the whole migration profile (*cf.* the energy values at 2.0 Å with those at 1.0 Å in Figures 4 and 5).

In considering alternatives, an apparent contradiction emerges. If, concurrent with methyl migration, there is loosening of the O-X bond to eventually give X<sup>-</sup>, then for configurations which are nearer to the product region, the energy minima on the projections along the O-X coordinate should occur at larger O-X values. Later configurations should be stabilized by longer O-X bonds. The calculations (Figures 4 and 5) do not indicate this. One reason for this apparent discrepancy would be that HX and not X<sup>-</sup> is lost. This loss of a neutral acid molecule rather than of an anionic species has been postulated before.<sup>1c,3</sup> The upward swing in energy in the *ab initio* curve (Figure 2) after 90% could then reflect the need to have longer O<sub>2</sub>-H<sub>9</sub> and O-X bonds in this region.

**Population Analysis.** To aid in the understanding of the energy profile, the gross atomic populations for all the configurations were computed as an extension of the *ab initio* study. These are featured in Table III.

Table III. Gross Atomic Populations<sup>a</sup>

Nucleus	% reaction						
	0	25	50	75	90	95	100
O <sub>1</sub>	8.3113	8.2948	8.2672	8.2832	8.1769	8.1777	8.1854
C <sub>2</sub>	5.9825	5.9533	5.9341	5.7977	6.2104	6.2728	6.3111
C <sub>3</sub>	6.5656	6.5526	6.5753	6.7717	6.4541	6.4197	6.3933
H <sub>4</sub>	0.7987	0.8347	0.8550	0.8363	0.8458	0.8257	0.8073
H <sub>5</sub>	0.8176	0.8487	0.8743	0.8538	0.8368	0.8149	0.8018
H <sub>6</sub>	0.8163	0.8441	0.8670	0.8429	0.8253	0.8025	0.7875
X, X = H	0.7924	0.7961	0.8122	0.8503	0.6405	0.6310	0.6313
H <sub>7</sub>	0.8326	0.8253	0.8106	0.8319	0.8713	0.8862	0.8945
O <sub>8</sub>	8.3201	8.3141	8.3006	8.2228	8.3647	8.3758	8.3831
H <sub>9</sub>	0.7727	0.7358	0.7036	0.7094	0.7743	0.7937	0.8047

<sup>a</sup> From *ab initio* calculations for rearrangement involving X = H.

The pattern of population changes must be interpreted with caution. The basis functions are limited and the analysis may tend to underestimate the formal popula-

tions on the atoms. Such errors should be systematic, however, and the relative values should be in the right order, even if the absolute values are not highly accurate. With this limitation in mind, some of the more salient features of Table III may be pointed out.

The most significant overall electron density changes observed (Figure 6) are on the atoms thought to be directly involved in migration: *viz.* the origin (C<sub>2</sub>), the terminus (O<sub>1</sub>), the carbon of the migrating methyl group (C<sub>3</sub>), the leaving group (H), and the hydroxyl oxygen (O<sub>8</sub>). Up to a certain point (75% migration), there is a flow of electron density from this hydroxyl oxygen. To a first approximation, this seems to concur with the assumption that the initial impetus for migration is provided by the lone pair electrons on this oxygen. From 0 to 75% migration, again, there is a smooth monotonic decrease in the atomic population on the migration origin (C<sub>2</sub>) and a buildup on the leaving group. The changes on the migrating carbon and the terminus follow an erratic pattern, but, in both cases, there is an initial loss in electron density (Table III).

On a very superficial level, then, it would seem that up to 75% migration there is an electron flow from the hydroxyl oxygen through the system to the leaving group, paralleling the "arrow-pushing" mechanism depicted in Scheme II. What is conflicting, however, is that there appears to be a buildup at certain positions along the way so that the electron population in the migrating group is *larger* at 75% migration than at the beginning of the reaction. This is probably a result of the O<sub>1</sub>-H bond being kept at 1.0 Å throughout the migration cross section.

#### Geometry Optimization of the Migration Maximum.

The  $\theta$  and  $\phi$  values, which were used for the configuration representing 75% migration, were kept constant, and the energy of the system was minimized (by CNDO/2) with respect to all the other independent internal coordinates. This was done principally to determine the nature of the hypersurface in this region, which is assumed to contain the transition state.

Notably, the cross sections along these coordinates were found to be represented by relatively shallow potential profiles compared with that for migration [*i.e.*,  $E(\theta, \phi, r(C_2O_1))$ ]. Changes in the bond lengths and bond angles cause relatively small changes in energy. Furthermore, most of the values originally assigned to these parameters, given the  $\theta$  and  $\phi$  necessary for 75% migration, proved to be their optimum values (Table II) at this point. This substantiates the original assumption, made in assigning intermediate geometries, that the changes in most of the parameters would be linearly dependent on percentage migration.

The optimized values presented in Table II should be those, or close to those, for the overall rearrangement transition state. It is tempting to attach chemical significance to the differences between these values and those for the reactant **1a** or product **3a**, also featured in Table II. There appears to be little change in the bond lengths and bond angles ( $\gamma$  and  $\angle HCH$ ) of the migrating methyl group. This is in complete agreement with the small  $\alpha$  isotope effects measured for the analogous Baeyer-Villiger rearrangement of phenyl-2-propanone.<sup>25</sup>

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The optimized C<sub>2</sub>-O<sub>8</sub> bond length is almost as short as that in **3a** (and hence in methyl formate) indicating that there is a partial carbonyl bond in the transition state. Experiments<sup>25</sup> with phenyl-2-propanone, again, yield  $\beta$  isotope effects, which are best interpreted in terms of partial re-formation in the rearrangement transition state of the carbonyl character, lost in the addition step (*cf.* Scheme I).

### Conclusion

A theoretical treatment of the reaction in Scheme II has yielded results which are in consistent agreement with experiment: the electronic nature of the leaving group affects the energy of the transition state; there is little reorganization in the migrating group; and the lone pair electrons on the hydroxylic oxygen of the

tetrahedral species (**1**) play a part in its rearrangement. These theoretical calculations have the additional advantage of providing information that would be difficult to obtain experimentally. On the basis of the model chosen, the rearrangement in the Baeyer-Villiger reaction is a concerted step, with the transition state occurring before a position 75% along the reaction coordinate. An ion pair intermediate has been excluded.

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## Thermal Isomerizations of 7-Alkoxy- and 7-Phenylbicyclo[2.2.1]heptadienes to Cycloheptatrienes<sup>1</sup>

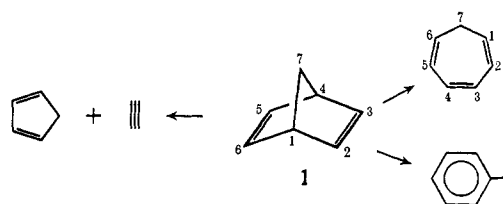
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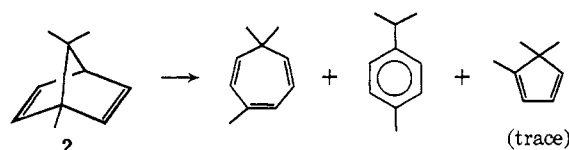
**Abstract:** 7-Alkoxy- and 7-phenylbicyclo[2.2.1]heptadienes rearrange nearly quantitatively to isomeric cycloheptatrienes. The isomerizations are kinetically first order with rates at 170° that are *ca.* 10<sup>6</sup> times that of the rearrangement of unsubstituted bicyclo[2.2.1]heptadiene to cycloheptatriene; the isomerization of 7-*tert*-butoxybicyclo[2.2.1]heptadiene has  $E_a = 35.5$  kcal/mol, 15 kcal/mol lower than that of unsubstituted bicyclo[2.2.1]heptadiene. The rate of isomerization of 7-*tert*-butoxybicyclo[2.2.1]heptadiene is not affected significantly by the polarity of the solvent, although isomerization in 2-ethoxyethanol furnishes 2-ethoxyethoxy- rather than *tert*-butoxycycloheptatrienes. The significance of these findings is discussed.

This paper describes the effects exerted by 7-alkoxy and 7-phenyl substituents upon the thermal reactions of norbornadiene (bicyclo[2.2.1]heptadiene, **1**). Heating norbornadiene at 320–475° furnishes cycloheptatriene, toluene, cyclopentadiene, and acetylene (Scheme I).<sup>5–9</sup> Although toluene also is obtained upon heating cycloheptatriene,<sup>5,10</sup> kinetic evidence suggests that it also can be formed directly from norbornadiene.<sup>9,10</sup> Not only is the rearrangement to cycloheptatriene greatly accelerated by 7-alkoxy or 7-phenyl substituents, but it becomes the only reaction observed, facilitating its study.

Scheme I



The thermal chemistry of other substituted norbornadienes has been investigated recently. Bornadiene (**2**) furnishes a mixture of products similar to that ob-



tained from the parent system (**1**).<sup>11,12</sup> However, the methyl substitution does lead to more rapid isomeriza-

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