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## Theoretical Studies on the Gas-Phase Wittig-Oxy-Cope Rearrangement of Deprotonated Diallyl Ether<sup>1</sup>

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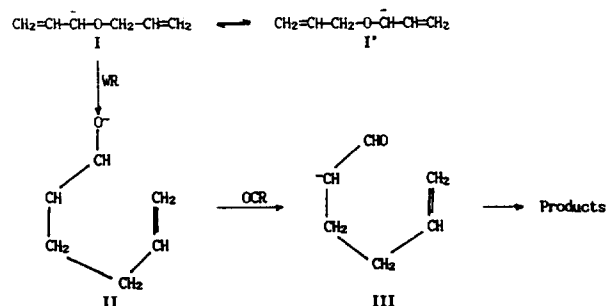
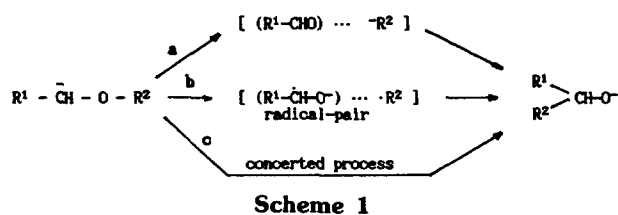
The Wittig-oxy-Cope rearrangements of deprotonated diallyl ether, I,  $\text{CH}_2=\bar{\text{C}}\text{H}-\text{CH}-\text{O}-\text{CH}_2-\text{CH}=\text{CH}_2$ , have been investigated theoretically by the AM1 method. A two step mechanism forming a Wittig product ion, II,  $(\text{CH}_2=\text{CH})(\text{CH}_2=\text{CH}-\text{CH}_2)\text{CHO}^-$ , through a radical-pair intermediate was found to provide the most favored reaction pathway in the Wittig rearrangement. The subsequent oxy-Cope rearrangement from species II also involves a two step mechanism through a biradicaloid intermediate. The intramolecular proton transfer in I (to form  $\text{CH}_2=\text{CH}-\text{CH}_2-\text{O}-\bar{\text{C}}\text{H}-\text{CH}=\text{CH}_2$ ) is a higher activation energy barrier process compared to the Wittig and oxy-Cope rearrangements and is considered to be insignificant. These results are in good agreement with the condensed-phase as well as gas-phase experimental results.

### Introduction

The Wittig rearrangement (WR)<sup>2</sup> has been extensively studied as one of the better known carbanion rearrangement in the condensed phase. Two-step mechanisms (reaction pathways *a* and *b*) involving either of the intermediate shown in Scheme 1 are proposed for the rearrangement.<sup>3</sup> However the possibility of a concerted one-step process (reaction pathways *c*) can not be entirely ruled out.<sup>4</sup> Various experimental results seem to support the two-step mechanism involving a radical pair, pathway *b*, rather than that involving an ionic intermediate, pathway *a*.<sup>5</sup> Some of the condensed-phase experimental results in favor of the radical-pair mechanism are: (i) the migratory aptitude of substituents  $\text{R}^2$  is in the order of free-radical stabilities,<sup>6</sup> allyl  $\cong$  benzyl > methyl > ethyl > phenyl, (ii) partial racemization of  $\text{R}^2$  is observed,<sup>7</sup> (iii) when ketyl radicals and R radicals from different precursors were brought together, similar products resulted.<sup>8</sup> Despite these experimental evidence in support of the radical-pair intermediate pathway, *b*, the radical mechanism is unable to account for all the reaction products and a concerted mechanism, *c*, is suggested as a possible alternative.<sup>4</sup> It is also known that when  $\text{R}^2$  is an allyl group, the [2,3] sigmatropic rearrangement can take place.<sup>9</sup>

The Wittig rearrangement can also occur in the gas-phase.<sup>10</sup> Eichinger *et al.*,<sup>10a</sup> have shown in their gas-phase studies on the Wittig rearrangement of deprotonated diallyl ether that (i) the proton-transfer reaction I to I' (Scheme 2) is insignificant, (ii) I undergoes facile reaction leading to 1,2- and 1,4-rearrangement products, (iii) the Wittig ions rearrange further by an oxy-Cope mechanism (OCR)<sup>11</sup> (Scheme 2).

In this work, we explore MO theoretically the most possi-

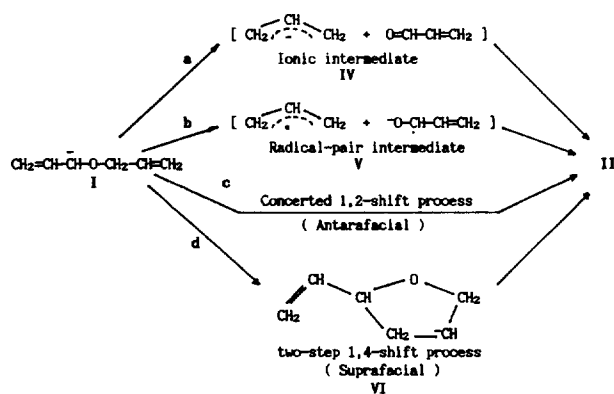


ble reaction pathway for the Wittig rearrangement of deprotonated diallyl ether (Scheme 1) and the mechanism of the subsequent oxy-Cope rearrangement of the Wittig product ion, II (Scheme 2).

### Computation

The AM1 procedure<sup>12</sup> implemented in AMPAC package<sup>13</sup> was used throughout in this work. The AM1 method accommodates some electron correlation effect through its parametrization<sup>14</sup> and it requires 2-3 orders of magnitude lesser computing time than even those using the relatively low level ab initio (3-21G) method.<sup>12,14</sup> It has been reported that AM1 gives good results for reactions of anionic species by giving

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efficient delocalization of negative charge,<sup>15</sup> and there are several works reported indicating that AM1 is the best mimic of the ab initio method in the computations of transition state (TS) geometries.<sup>16</sup>

In this work, for ionic processes the RHF method was used and for radical processes the UHF procedure was adopted. For energies and geometries of equilibrium points, *i.e.*, ground states (GS), intermediates (IM) and products (P), full optimization with respect to all geometrical parameters was carried out. In the determination of the TS structures and energies, a TS position along the reaction coordinate was initially approximated,<sup>17</sup> refined it by gradient norm minimization<sup>18</sup> and characterized by confirming only one negative eigenvalue in the Hessian matrix.<sup>19</sup>

## Results and Discussion

**Wittig Rearrangement of Deprotonated Diallyl Ether, I.** For the Wittig rearrangement of I to II, four possible processes shown in Scheme 3 are considered. This rearrangement proceeds exothermically since the heat of formation ( $\Delta H_f$ ) of II is lower by 11.5 kcal/mol than that of I.

The 1,2-shift pathway in Scheme 3 is a concerted one-step process and hence differs from the other three processes involving intermediate or intermediate complex. In this work, we were unable to obtain the TS structure for this one-step process. We can think of two reasons for this failure: (i) the TS conceivable for this concerted 1,2-shift process would be a three-membered ring structure which is highly strained<sup>20</sup> and hence requires a high activation energy, (ii) the Perturbation MO (PMO)<sup>21</sup> approach indicates that such a TS is difficult to envisage since orbital overlap in a front-side  $S_N2$  attack is very inefficient. Furthermore any thermal 1,2-shift should proceed in an antarafacial fashion making the orbital overlap even more difficult.<sup>22</sup>

The heats of formation ( $\Delta H_f$ ) of stationary points on all reaction pathways except those for the 1,2-shift are summarized in Table 1. Reference to this Table reveals that in all three reaction paths the first step, *i.e.*, formation of intermediate, is rate limiting, the radical-pair process being the most favored among the three. Several factors seem to contribute to this preference of the radical-pair process over the ionic intermediate and 1,4-shift processes. In the radical-pair process 2-propenone radical anion and an allyl radical are formed whereas in the ionic intermediate process 2-propenone

**Table 1.** Heats of formation ( $\Delta H_f$ ) of Stationary Point Species for the Wittig Rearrangement Process in kcal/mol

Path	I	TS(1)	IM(1)	TS(2)	II	$\Delta H^*(1)^a$	$\Delta H^*(2)^b$
a		+15.8	-1.3	+2.5		18.7	5.5
b	-3.0	+7.2	-4.8	-1.8	-14.6	10.2	1.2
d		+8.4	-7.1	+6.2		11.4	9.2

<sup>a</sup>  $\Delta H^*(1) = \Delta H_f(\text{TS}(1)) - \Delta H_f(\text{I})$ . <sup>b</sup>  $\Delta H^*(2) = \Delta H_f(\text{TS}(2)) - \Delta H_f(\text{I})$ .

and an allyl anion are produced. Since the  $\pi$ -HOMOs for the allyl radical and anion are the (same) nonbonding MO (NBMO),<sup>23</sup> there will be no difference in stability between the allyl radical and anion. Therefore the difference in  $\Delta H^*$  between the two processes can be ascribed to the difference in stabilities of the other intermediate, *i.e.*, 2-propenone and 2-propenone radical anion.

2-Propenone in the ionic process is a  $4\pi$ -electron system, whereas 2-propenone radical anion in the radical process is a  $5\pi$ -electron system; since through space interaction of  $5\pi$ -electron system is known to be more stabilizing than that of  $4\pi$ -electron system,<sup>24</sup> the radical anion should be the more stable species. On the other hand, inspection of TS geometries in Figure 1 reveals that the extent of C-O bond cleavage in the TS is greater for the ionic process than that for the radical process leading to a higher activation energy for the former process due to a greater amount of deformation energy required.

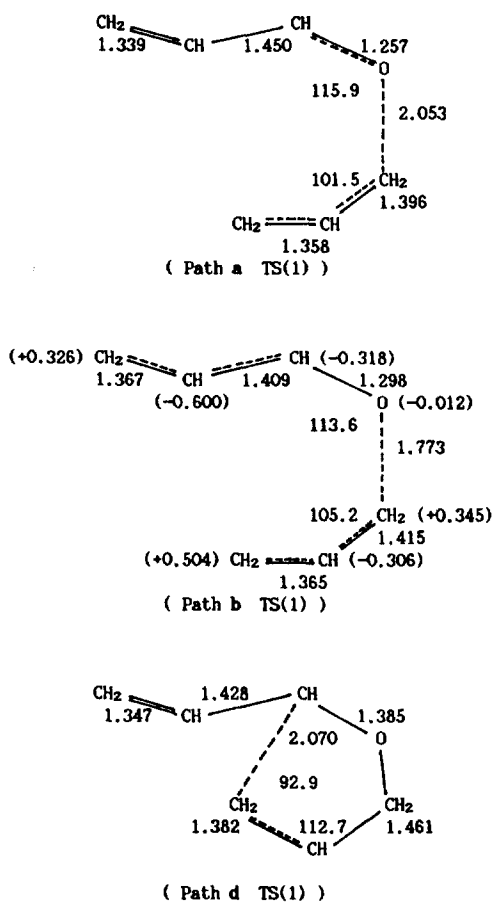
The second steps, proceeding from intermediates to II subsequent to the rate-determining steps, are all relatively fast so that the overall reaction rates are not influenced by them. Nevertheless, radical recombination in the radical-pair process will also be the most favored one among the second steps for the three pathways. The TS structures corresponding to the first step are presented in Figure 1.

**Oxy-Cope Rearrangement of Wittig Product Ion, II.** The oxy-Cope process<sup>11</sup> is a kind of the well-known Cope rearrangement<sup>25</sup> in which aldehyde or ketone is produced as a product. The oxy-Cope rearrangement is not reversible, however, in contrast to the normal Cope rearrangement.<sup>11</sup>

The Wittig product ion, II, has a negative charge developed on the oxygen atom and the oxy-Cope rearrangement is known to proceed very rapidly forming an enolate anion.<sup>26</sup> Our AM1 results indicate that the process from II is exothermic by 25.8 kcal/mol, which is consistent with the irreversibility observed experimentally. Moreover, our results predict a two-step process involving a biradical intermediate, which is in accord with the similar biradical two-step mechanism proposed for the Cope rearrangement by Doering *et al.*<sup>27</sup> and Dewar *et al.*<sup>28</sup>

The heats of formation ( $\Delta H_f$ ) of stationary points for the oxy-Cope rearrangement, II  $\rightarrow$  P, are summarized in Table 2. Examination of this Table shows that the first step, in which biradical intermediate VII (Figure 3) is formed, is rate-limiting and the following second step is rapid. This is because species VII is relatively unstable compared to the intermediate, II, and product, P.

Examination of potential energy profile for the overall process from the reactant, I, to the product, P, in Figure 2 reveals that the rate-determining step for the entire course



**Figure 1.** Geometries of TS(1) for the Wittig rearrangement process (Bond lengths and angles are in Å and degree). Group spin densities for radical process are shown in parenthesis for pathways b.

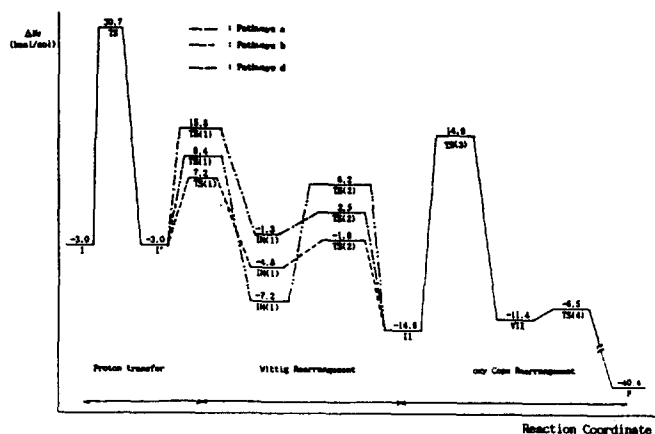
**Table 2.** Heats of Formation ( $\Delta H_f$ ) of Stationary Point Species for the oxy Cope Rearrangement Process in kcal/mol

II	TS(3)	VII	TS(4)	P. C.	$\Delta H^*(3)^a$
-14.6	+14.9	-11.4	-8.5	-40.4	17.9

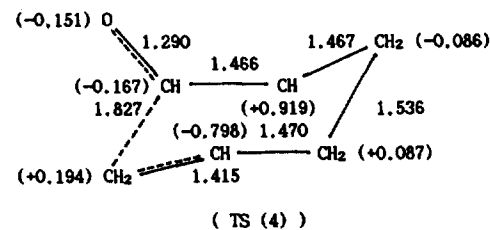
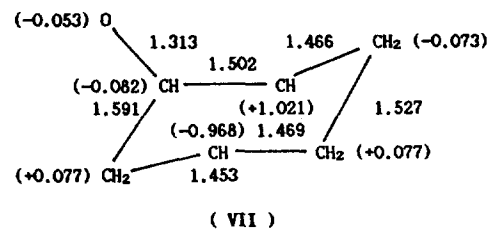
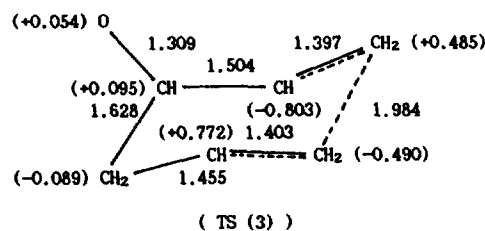
$$^a \Delta H^*(3) = \Delta H_f(\text{TS}(3)) - \Delta H_f(\text{I}).$$

of reaction is the first step in the oxy-Cope rearrangement. This means that the Wittig rearrangement, I $\rightarrow$ II, prior to the oxy-Cope process, II $\rightarrow$ P, takes place in a pre-equilibrium. The structures of the TSs and biradical intermediate for the oxy-Cope process are shown in Figure 3.

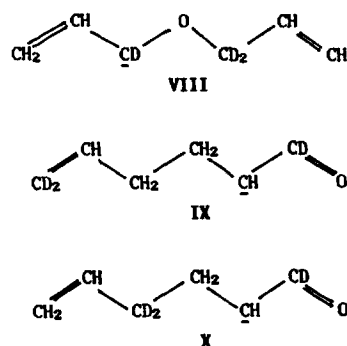
**Comparison with the Gas-Phase Experimental Results.** The results of the gas-phase experiment involving deuterated diallyl anion, VIII, by Eichinger *et al.*<sup>10a</sup> have shown that the product ratio of IX to X is 1 : 1. The radical-pair mechanism, which was predicted to be of the most preferred, is perfectly compatible with this experimental fact; the allyl radical which is one of the radical pair, V, can delocalize to form  $C_\alpha H_2=C=C_\beta D_2$ , XI, and in the radical recombination with 2-propene radical ion two terminal carbon atoms,  $C_\alpha$  and  $C_\beta$ , will have equal chance of bond formation so that the 1 : 1 ratio of IX to X should result. On the other hand, they found with deuterated species XII that the intra-



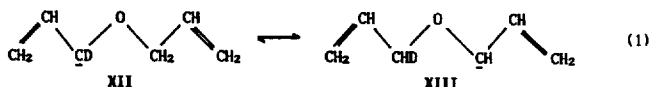
**Figure 2.** Potential energy profile for the Wittig-oxy-Cope rearrangement of diallyl ether anion, I.



**Figure 3.** Geometries of TSs and intermediate for the oxy-Cope rearrangement process (Bond lengths and angles are in Å and degree). Group spin densities are shown in parenthesis.



molecular proton transfer process, XII→XIII (Eq. 1), does not compete effectively with other rearrangements. Our result of the high activation energy barrier found for this process ( $\Delta H^\ddagger \cong 34$  kcal/mol) in Figure 2 is again consistent with the experimental result.<sup>10</sup>



The results of our AM1 studies can be summarized as follows: (i) The Wittig rearrangement of deprotonated diallyl anion, I, proceeds by a two-step radical mechanism. (ii) The oxy-Cope rearrangement of 3-hydroxy-1,5-hexadiene anion, II, takes place in a two-step process involving biradical intermediate VII. (iii) The rate-determining step for the overall reaction is the first step in the oxy-Cope process subsequent to the Wittig rearrangement. (iv) The intramolecular proton transfer within the reactant, I, is a higher energy barrier process compared to the Wittig as well as oxy-Cope rearrangements.

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