JOURNAL OF PHYSICAL ORGANIC CHEMISTRY, VOL. 5, 812–818 (1992)

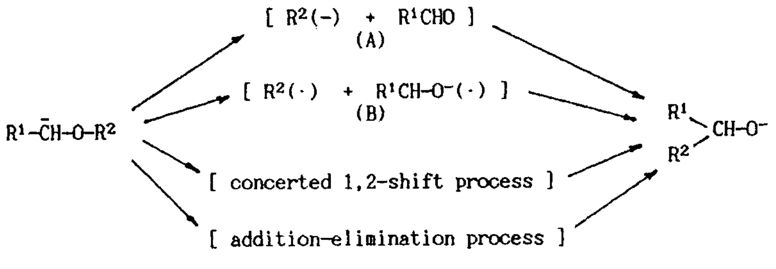
THEORETICAL STUDIES ON THE GAS-PHASE REARRANGEMENT OF DEPROTONATED ALLYL PHENYL ETHER*

CHANG KON KIM, BON-SU LEE AND IKCHOON LEE†
Department of Chemistry, Inha University, Inchon 402-751, Korea

The Wittig and anoinic Claisen rearrangements of deprotonated allyl phenyl ether, $PhO\bar{C}HCH=CH_2$, were investigated by MO theory employing the AM1 method. The most favoured reaction pathway for the Wittig rearrangement is the intramolecular S_NAr process proceeding by the addition – elimination mechanism involving a Meisenheimer complex-type, three-membered-ring intermediate. For the anionic Claisen rearrangement a three-step mechanism is favoured, in which the intramolecular proton transfer occurs first from the *ortho* position of the phenyl ring to the anionic carbon centre, which is then followed by a process involving a six-membered ring intermediate. The two types of rearrangements can compete, but the Wittig type is more facile and favoured than the Claisen process owing to the lower activation enthalpy. The results are in good agreement with gas-phase experimental results.

INTRODUCTION

The Wittig rearrangement (WR)[2] is one of the well known carbanion rearrangements that have been studied extensively in the condensed phase. The reaction is considered to proceed in a two-step process involving either an ion–neutral (A) or a radical-pair (B) intermediate as shown in Scheme 1.[3] In addition, a variety of other mechanisms, such as a one-step concerted 1,2-shift type process and an addition–elimination process depending on the structure of R^1 and R^2 groups, are also conceivable.[4] However, it has been suggested that the radical-pair mechanism, (B in Scheme 1) is the more likely, based on condensed-phase experimental results:[5] (i) aldehydes are often observed as by-products of the reaction; (ii) the migratory aptitude of substituent R^1 decreases in the order allyl ⩾ benzyl > methyl > ethyl > phenyl, which is not the order of anionic stabilities but is the order of free-radical stabilities;[6] (iii) partial racemization of R^2 is observed;[7] and (iv) similar products are produced when ketyl and R· radicals are formed from other precursors.[8] Despite this experimental evidence, in some cases the radical process alone cannot account for all the products and the possible involvement of other ionic process has been reported.[9]



Scheme 1

---

* Determination of Reactivity by MO Theory, Part 80. For Part 79, see Ref. 1.
† Author for correspondence.

0894–3230/92/120812–07$08.50

Received 25 March 1992
Revised 12 June 1992

The Wittig rearrangement also occurs in the gas phase;[10] work in this field has not been as extensive as the solution-phase studies. In this work, we investigated theoretically all conceivable reaction pathways of the WR of deprotonated allyl phenyl ether (I) to the Wittig product ion (II) using the AM1 method.[11] These theoretical results were compared with the experimental results of Eichinger and Bowie[10a] and also with previous theoretical work on the WR of deprotonated diallyl ether.[12] Since ally phenyl ether (I) can also form *o*-allylphenolate anions (III) in an anionic Claisen rearrangement (CR)[13], [equation (1)], we also investigated the mechanism of this CR process in addition to the major WR process.

(I) (III) (1)

CALCULATIONS

The AM1 procedure implemented in the AMPAC package[14] was used throughout. The AM1 method accommodates some electron correlation effects through its parameterization[15] and it requires 2–3 orders of magnitude less computing time than even those using the relatively low level *ab initio* (3–21G) method.[11,15] It has been reported that AM1 gives good results for reactions of anionic species by giving efficient delocalization of negative charge,[16] and there are several reports indicating that AM1 is the best mimic of the *ab initio* method in the computations of transition-state (TS) geometries.[17]

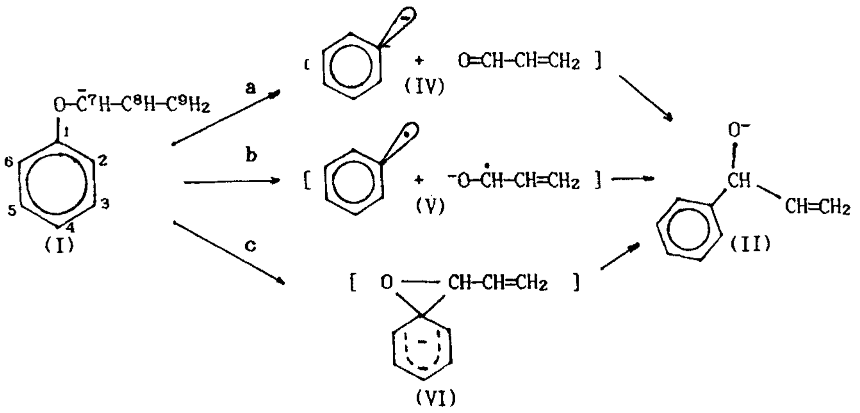
In this work, for ionic processes the RHF method was used and for radical processes the UHF procedure was adopted. For energies and geometries of equilibrium points, i.e. ground state (GS), intermediates (IM) and products (P), full optimization with respect to all geometrical parameters was carried out. In the determination of the TS structures and energies, a TS position along the reaction coordinate was initially approximated,[18] refined by gradient norm minimization[19] and characterized by confirming only one negative eigenvalue in the Hessian matrix.[20]

RESULTS AND DISCUSSION

Wittig rearrangement of deprotonated allyl phenyl ether (I)

The three reaction pathways, (a)–(c), in Scheme 2 are conceivable for the Wittig rearrangement of deprotonated allyl phenyl ether (I) to the Wittig product ion (II): (a) an ionic process through an ion–neutral complex (IV); (b) a radical process through a radical-pair intermediate (V); or (c) an addition–elimination process by the intramolecular S$_{\mathrm{N}}$Ar mechanism through a three-membered ring, Meisenheimer complex-type intermediate (VI).

Reference to potential energy profiles in Figure 1 indicates that the pathway (c) through species VI is the most favourable process with the rate-limiting addition of the C-7 atom to the *ipso*-carbon of the phenyl ring. A relatively lower energy barrier is provided in process (c) by the more favourable electronic effect, which can more than compensate for the unfavourable steric effect. Intermediate VI formed in the rate-determining step of pathway (c) contains a sterically strained three-membered ring in contrast to a simple heterolysis of the Ph—O bond in pathway (a) and a homolysis in pathway (b). On the other hand, however, reference to the ground-state (GS) and transition-state (TS) atomic charge densities in Table 1 reveals that in the pathway



Scheme 2

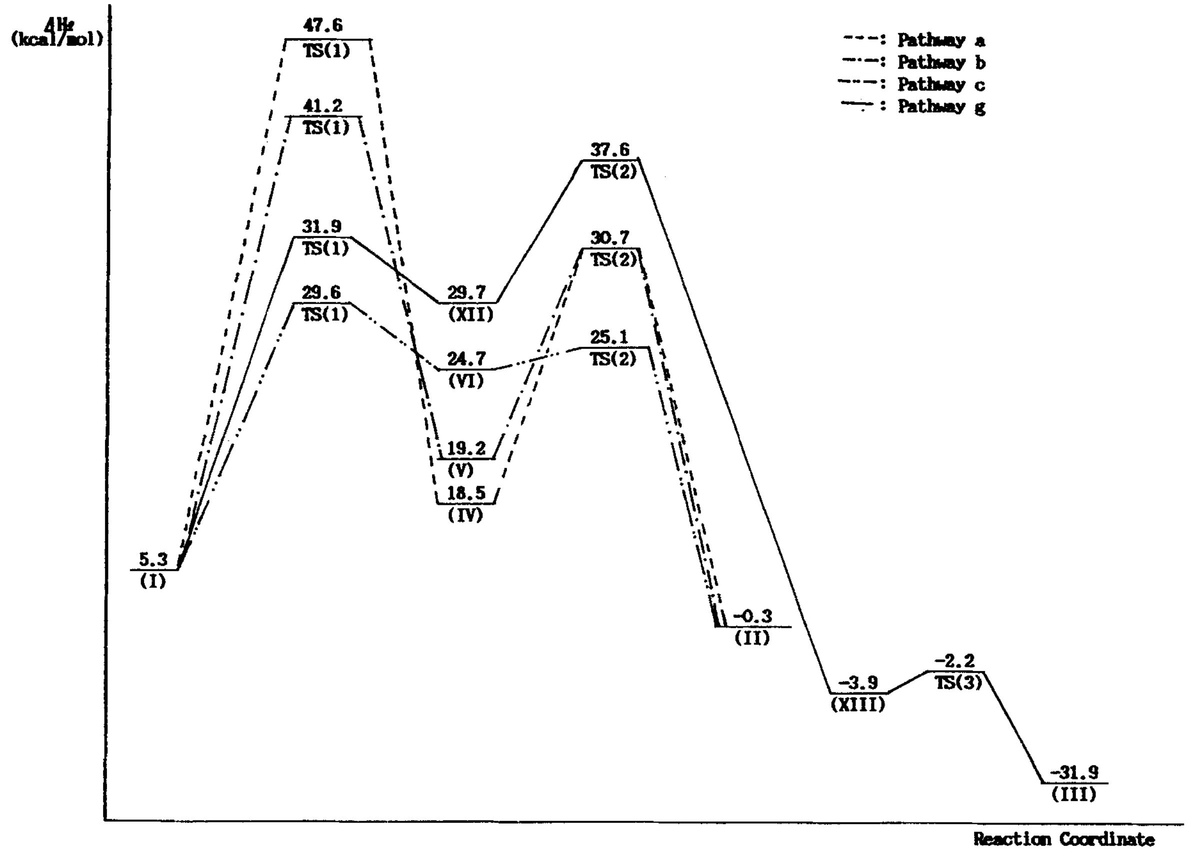


Figure 1. Potential energy profile for the Wittig and anionic Claisen rearrangement of ally phenol ether anion, I

(c) negative charge is delocalized only within an allyl fragment in the GS, whereas it becomes dispersed over the entire molecule due to charge transfer into the phenyl ring in the TS.

This enhanced charge delocalization in the TS leads to a lowering of the activation energy barrier for the pathway (c). In contrast, in the pathways (a) and (b) negative charge (or an unpaired electron) is localized on the *ipso*-carbon of the phenyl ring (C-1) in a σ-type complex (Table 1) as a phenyl anion [Δq(C-1) = −0·482] or a phenyl radical [Δq(C-1) = −0·094 and spin density of C-1 = + 1·282] is formed in the TS.

Table 1. Charge density (q) of the heavy atoms for the first-step TS of the Wittig rearrangement process in electronic units

	O	C-7	C-8	C-9	C-1	C-2	C-3	C-4	C-5	C-6
GS	−0·120	−0·495	+0·027	−0·538	+0·103	−0·212	−0·204	−0·111	−0·107	−0·225
TS(A)	−0·158	+0·110	−0·166	−0·254	−0·379	−0·157	−0·174	−0·168	−0·164	−0·230
Δq[a]	−0·038	+0·605	−0·193	+0·284	−0·482	+0·055	+0·030	−0·057	−0·057	−0·005
TS(B)	−0·505	+0·064	−0·332	−0·386	+0·009	−0·140	−0·111	−0·153	−0·148	−0·173
Δq[a]	−0·385	+0·559	−0·359	+0·152	−0·094	+0·072	+0·093	−0·042	−0·041	+0·052
GSD[b]	−0·219	−0·176	+0·115	−0·667	+1·282	−0·381	−0·391	+0·412	+0·403	−0·374
TS(C)	−0·242	−0·352	−0·022	−0·402	+0·238	−0·296	−0·290	−0·057	−0·058	−0·328
Δq[a]	−0·122	+0·143	−0·049	+0·136	+0·135	−0·084	−0·086	+0·054	+0·049	−0·103

[a] $\Delta q = \Delta q(\text{TS}) - \Delta q(\text{GS})$.
[b] Group spin density for TS.

Moreover, in pathway (b) negative charge becomes localized on the oxygen atom (Table 1) of the prop-2-enol radical anion in the TS, in contrast to a more delocalised allyl fragment in the GS.

Another aspect of the favourable electronic effect is a greater charge-transfer stabilization[21] of the TS ($\mathscr{E}_{ct}$). One factor determining $\mathscr{E}_{ct}$ is the energy gap ($\Delta\mathscr{E}$) of the frontier molecular orbital (FMOs); the narrower the gap, the greater is the charge-transfer stabilization in the TS. In both pathways (a) and (b), the first step, Ph—O bond cleavage, is rate limiting; the inter-frontier level gap, $\Delta\mathscr{E}$, is 7·87 eV for this step since the HOMO is the non-bonding MO (NBMO) of the allyl fragment and the LUMO is the antibonding MO (σ^*) of the Ph—O bond in these two pathways. However, for pathway (c) the energy gap is much lower, $\Delta\mathscr{E} = 4{\cdot}27$ eV, owing to the lower LUMO which is the π^* orbital of the phenyl ring. This narrowing of the inter-frontier orbital gap by 3·60 eV for process (c) compared with the other two processes results in a greater charge-transfer stabilization, providing a lower activation energy barrier path.

Pathway (b) is more favourable than (a) owing to a greater negative charge dispersion effect, even though the steric effect in the rate-limiting Ph—O bond scission, a simple heterolysis and homolysis, respectively, is similar in both (a) and (b). In (a) the negative charge is localized on the *ipso*-carbon atom (C-1) in the TS, whereas in (b) it is localized on the more electronegative atom, O. Further, the intermediate in pathway (b), prop-2-enone radical anion (V), forms a 5-π-electron system which is more stable than a 4-π-system of the intermediate in (a), prop-2-enone (IV).[12,22] Hence the activation barrier increases in the order pathway (c) < (b) < (a). The TS geometries for the rate-determining (first) step in the three reaction pathways are shown in Figure 2.

The subsequent product formation steps from the respective intermediates, IV–VI, are all fast compared with the rate-limiting first steps and hence have no effect on the reactivity, but the barrier height involved in process (c) is nonetheless the lowest.

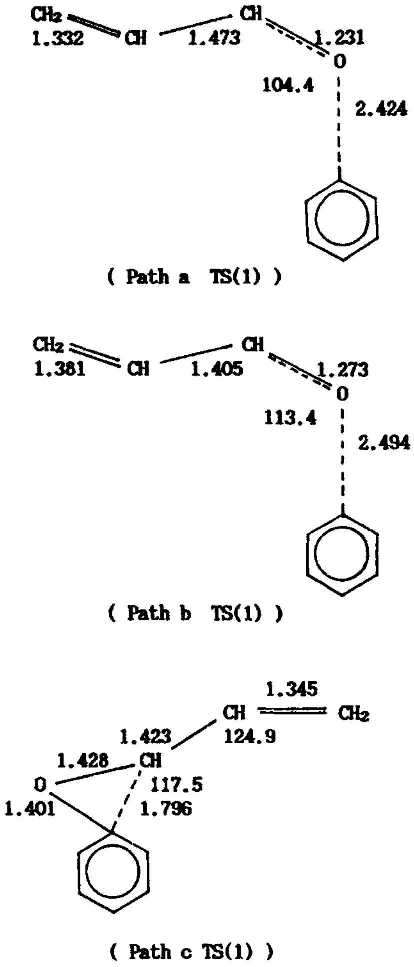
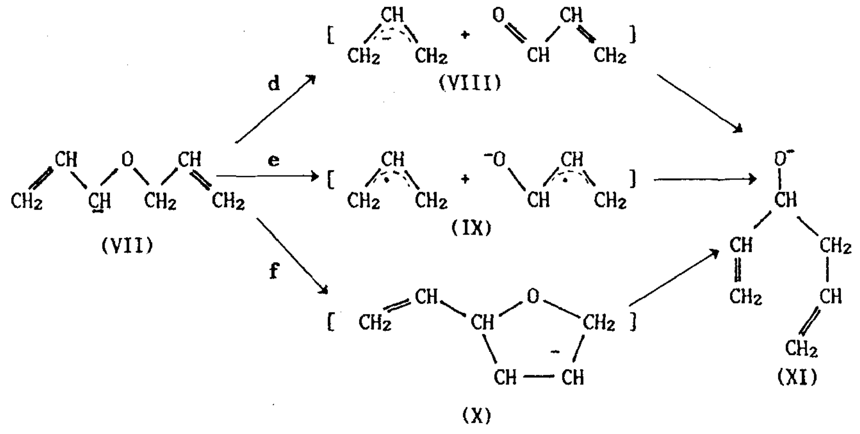


Figure 2. Geometries of TS(1) for the Wittig rearrangement process (bond lengths in Å and angles in degrees)

The Wittig rearrangement mechanism for the deprotonated allyl phenyl ether (I) discussed above is different from that reported for the deprotonated diallyl ether (VII);[12] for the former, the reaction is expected to proceed by pathway (c) with an S_NAr-type addition–elimination mechanism, whereas for the latter, the radical process, pathway (e), in Scheme 3 is the most favourable among the three possible mechanisms. This difference in mechanism for I and VII can easily be accounted for by the difference in stabilities of the two radical pair intermediates V and IX, respectively which are formed in the rate-determining step. Since prop-2-enone radical anion is common to the two intermediates V and IX, the relative stability of the other radical, i.e phenyl and allyl radicals, mainly contributes to the difference in the mechanism. According to the conventional stabilization energy,' SE°, in equation (2), proposed by Cox and Pilcher:[23]

$$SE^\circ = \Delta H_a^\circ - \sum_i \mathscr{E}_i^\circ \qquad (2)$$

where SE° = stabilization energy, ΔH_a° = heat of atomization of the species, experimentally determined or theoretically estimated, and $\Sigma_i \mathscr{E}_i^\circ$ = heat of atomization calculated using standard bond energies corresponding to an arbitrary chemical formula of the compound, the phenyl radical is destabilizing by 10·3 kcal mol^{-1} (1 kcal = 4·184 kJ), whereas the allyl radical is stabilizing by 13·3 kcal mol^{-1}.[24] Owing to this difference in the relative stabilities of the two intermediate radicals, the diallyl ether anion (VII) can



Scheme 3

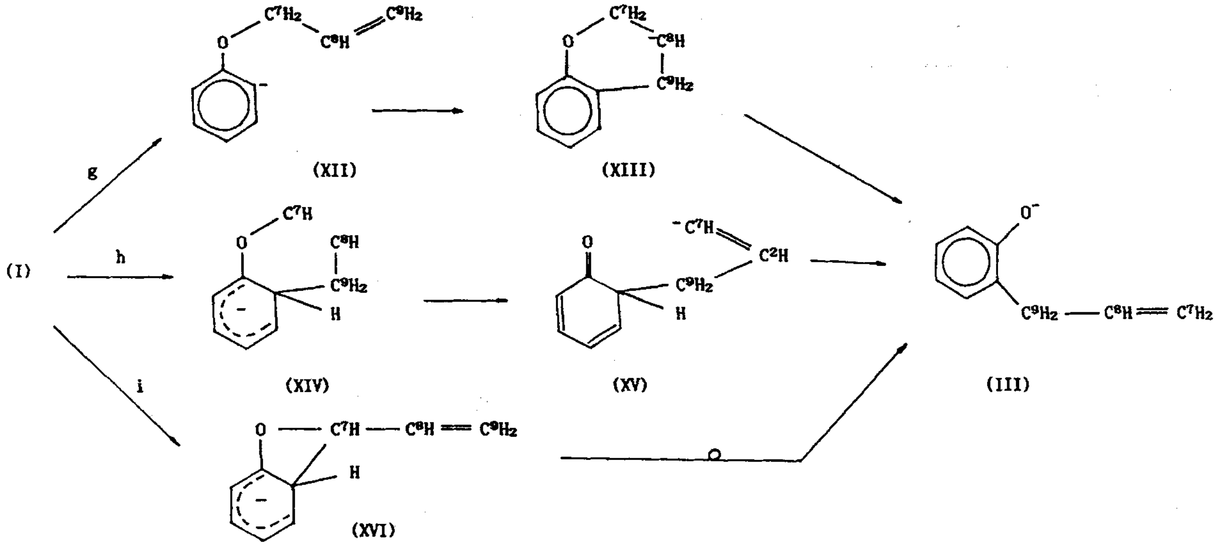
proceed via the radical process with the lowest barrier of $\Delta H^{\neq} = 10{\cdot}2\ \text{kcal mol}^{-1}$, path (e) in Scheme 3, but for the allyl phenyl anion (I) the radical process, path (b) in Scheme 2, has a barrier of $\Delta H^{\neq} = 35{\cdot}9\ \text{kcal mol}^{-1}$, which is higher by $25{\cdot}7\ \text{kcal mol}^{-1}$ than the corresponding radical process involving the diallyl ether anion and by $14{\cdot}1\ \text{kcal mol}^{-1}$ than the most favoured pathway (c) in Scheme 2. The difference in barriers of $\delta\Delta H^{\neq} = 25{\cdot}7\ \text{kcal mol}^{-1}$ between the two radical processes for compounds I and VII arises almost entirely from the difference in the relative stabilities of radical stabilization energy, $\Delta SE^{\circ} = SE^{\circ}(\text{allyl}) - SE^{\circ}(\text{phenyl}) = 23{\cdot}6\ \text{kcal mol}^{-1}$. In other words, owing to this destabilization of the phenyl radical involved in path (b), the addition–elimination process ($\Delta H^{\neq} = 24{\cdot}3\ \text{kcal mol}^{-1}$) can be the lowest energy barrier path for I. Even though the addition–elimination mechanism provides the most favoured pathway (c) for the Wittig rearrangement of I, the activation barrier is higher by $14{\cdot}1\ \text{kcal mol}^{-1}$ $[= \Delta H^{\neq}(\text{I}) - \Delta H^{\neq}(\text{VII})]$ than the radical Wittig rearrangement of VII, in agreement with the experimental migratory aptitude of R^2 in solution, allyl > phenyl.[6]

Anionic Claisen rearrangement of deprotonated allyl phenyl ether (I)

The deprotonated allyl phenyl ether anion (I) can produce the rearranged product, *o*-allylphenolate anion (III), in the anionic Claisen rearrangement[13] (CR) processes shown in Scheme 4. Reference to the potential energy profile in Figure 1 indicates that the three-step mechanism, pathway (g), is most favoured. In pathway (i), a sterically strained intermediate (XVI) with a four-membered ring is formed in the rate-determining step. The four-membered ring in this intermediate is highly strained[25] and should have more ring strain than that involving sp^3-hybridized orbitals. The C-1 atom of the phenyl ring is sp^2 hybridized, so that the angle $\angle$O—C-1—C-6 should be *ca* 120° in order to minimize the ring strain, but the optimized angle of $\angle$O—C-1—C-6 turned out to be 94·9°. This angle strain will be greater than that may be encountered in an sp^3-hybridized ring. The high ring strain is reflected in the high heat of formation, $\Delta H_f = 41{\cdot}6\ \text{kcal mol}^{-1}$, of the intermediate XVI, which is higher than the barrier height of TS (2) involved in the rate-determining step of path (g), $\Delta H_f = 37{\cdot}6\ \text{kcal mol}^{-1}$. Hence the barrier height for the TS in path (i) should be substantially higher than that of TS (2) in path (g), so we did not pursue the process (i) any further. Similarly, path (h) also has a high-energy intermediate (XV), with $\Delta H_f = 49{\cdot}7\ \text{kcal mol}^{-1}$ which is higher than the barrier height for the TS (2) of path (g), suggesting a still higher activation barrier for the TS in the process XIV → XV. The only plausible process involved in the anionic Claisen rearrangement in Scheme 4 is therefore pathway (g), a three-step process. This is in agreement with the mechanism proposed by Eichinger *et al.*[10a] based on gas-phase experiments. The TS geometries for the pathway (g) are shown in Figure 3.

On the other hand, examination of potential energy profiles in Figure 1 shows that path (c) for the WR process is more favoured than path (g) for the CR process, which is also in agreement with the gas-phase results of Eichinger *et al.*[10a]

We conclude that (i) the most favoured pathway for the Wittig rearrangement of deprotonated allyl phenyl ether is the two-step mechanism in which first addition of the α-carbon atom (α to O) of the allyl fragment occurs at the *ipso* position (C-1) of the phenyl ring, and then elimination via breaking of the O—C-1 bond takes place; (ii) the most favourable process for the anionic



Scheme 4

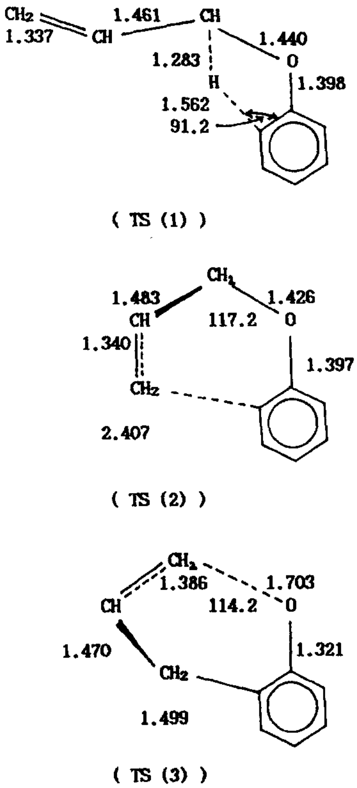


Figure 3. Geometries of TSs for pathway (g) of the anionic Claisen rearrangement process (bond lengths in Å and angles in degrees)

rearrangement is the three-step mechanism in which the *ortho*-hydrogen of the phenyl ring is first transferred to the α-carbon of the allyl fragment and then addition of γ-carbon takes place at the *ortho* position, which is followed by O—C-α bond cleavage; and (iii) the two rearrangements, WR and CR, may compete but the Wittig rearrangement is more facile and hence more favoured than the Claisen rearrangement.

ACKNOWLEDGEMENTS

We thank the Korea Science and Engineering Foundation and the Ministry of Education for support of this work.

REFERENCES

1. B. S. Park. I. Lee, J. K. Cho and C. K. Kim, *J. Korean Chem. Soc.* **36**, 366 (1992).
2. (a) G. Wittig, *Angew. Chem.* **66**, 10 (1954); (b) H. E. Zimmerman, in *Molecular Rearrangements*, edited by P. de Mayo, Vol. 1, p. 345. Interscience, London (1963); (c) J. E. Baldwin, J. de Bernardis and J. E. Patrick, *Tetrahedron Lett.* 353 (1970).
3. (a) C. R. Hauser and S. W. Kantor, *J. Am. Chem. Soc.* **73**, 1437 (1951); (b) J. Cast, T. S. Stevens and J. Holmes, *J. Chem Soc.* 3521 (1960).
4. J. F. Garst and C. D. Smith, *J. Am. Chem. Soc.* **98**, 1526 (1976); for evidence against this, see E. Hebert, Z. Welvart, M. Ghelfenstein and H. Szware, *Tetrahedron Lett.* **24**, 1381 (1983).
5. (a) U. Schöllkopf, *Angew. Chem., Int. Ed. Engl.* **9**, 763 (1970); (b) J. J. Eisch, C. A. Kovacs and S. Rhee, *J. Organomet. Chem.* **65**, 289 (1974).

6. (a) P. T. Lansbury, V. A. Pattison, J. D. Sidler and J. B. Bieber, *J. Am. Chem. Soc.* **88**, 78 (1966); (b) H. Schäfer, U. Schöllkopf and D. W. Walter, *Tetrahedron Lett.* 2809 (1968).
7. (a) U. Schöllkopf and W. Fabian, *Justus Liebigs Ann. Chem.* **642**, 1 (1961); (b) U. Schöllkopf and H. Schäfer, *Justus Liebigs Ann. Chem.* **663**, 22 (1963); (c) H. Felkin and C. Frajerman, *Tetrahedron Lett.* 3485 (1977); (d) E. Hebert and Z. Welvart, *J. Chem. Soc., Chem. Commun.* 1035 (1980).
8. J. F. Garst and C. D. Smith, *J. Am. Chem. Soc.* **95**, 6870 (1973).
9. (a) J. E. Baldwin and J. E. Patrick, *J. Am. Chem. Soc.* **93**, 3556 (1971); (b) A. F. Thomas and R. Dubini, *Helv. Chim. Acta*, **57**, 2084 (1974); (c) K. Mikami, S. Taya and Y. Fujita, *J. Org. Chem*, **46**, 5447 (1981).
10. (a) P. C. H. Eichinger and J. H. Bowie, *J. Chem. Soc., Perkin Trans. 2* 497 (1988); (b) P. C. H. Eichinger and H. Bowie, *J. Chem. Soc., Perkin Trans. 2* 1499 (1987); (c) P. C. H. Eichinger, J. H. Bowie and T. Blumenthal, *J. Org. Chem*, **51**, 5078 (1986).
11. M. J. S. Dewar, E. G. Zoebisch, E. F. Healy and J. J. P. Stewart, *J. Am. Chem. Soc.* **107**, 3902 (1985).
12. C. K. Kim, I. Lee, H. W. Lee and B.-S. Lee, *Bull. Korean Chem. Soc.* **12**, 678 (1991).
13. R. P. Lutz, *Chem. Rev.* **84**, 205 (1984).
14. M. J. S. Dewar, *AMPAC: Austin Model 1 Package.* QCPE No. 506.
15. M. J. S. Dewar, A. J. Holder, E. F. Healy and S. Olivella, *J. Chem. Soc. Chem. Commun.* 1452 (1989).
16. (a) M. J. S. Dewar and Y.-C. Yuan, *J. Am. Chem. Soc.* **112**, 2088 (1990); (b) S. Hoz, K. Yang and S. Wolfe, *J. Am. Chem. Soc.* **112**, 1319 (1990).
17. (a) D. C. Spellmeyer and K. N. Houk, *J. Am. Chem. Soc.* **110**, 3412 (1988); (b) M. J. S. Dewar, E. F. Healy, *Chem. Phys. Lett.* **141**, 521 (1987); (c) M. J. S. Dewar and B. M. O'Connor, *Chem. Phys. Lett.* **138**, 141 (1987); (d) M. Müller and G. Hohlneicher, *J. Am. Chem. Soc.* **112**, 1273 (1990).
18. M. J. S. Debar and S. Kirschner, *J. Am. Chem. Soc.* **93**, 4290 (1971).
19. (a) A. Komornicki, K. Ishida and K. Morokuma, *Chem. Phys. Lett.* **45**, 595 (1979); (b) J. W. McIver, Jr, and A. Komornicki, *J. Am. Chem. Soc.* **94**, 2625 (1972).
20. I. G. Csizmadia, *Theory and Practice of MO Calculations on Organic Molecules*, p. 239. Elsevier, Amsterdam (1976).
21. (a) L. Salem, *J. Am. Chem. Soc.* **90**, 543 (1968); (b) K. Fukui and H. Fujimoto, *Bull. Chem. Soc. Jpn.* **41**, 1989 (1968).
22. I. Lee, B.-S. Lee and K. Yang, *Bull. Korean Chem. Soc.* **4**, 157 (1983).
23. J. D. Cox and G. Pilcher, *Thermochemistry of Organic and Organometallic Compounds*, Academic Press, London (1970).
24. R. Daudel, G. Leroy, D. Peeters and M. Sana, *Quantum Chemistry*, Chapt. 6. Wiley, New York (1983).
25. (a) J. F. Liebman and A. Greenberg, *Chem. Rev.* **76**, 311 (1976); (b) I. Lee and C. K. Kim, *J. Comput. Chem.* **11**, 1119 (1990); (c) I. Lee, C. K. Kim, B. H. Kong and B. C. Lee, *J. Phys. Org. Chem.* **4**, 449 (1991).