H, at C_5), 3.6 (m, 1 H, at C_8), 4.9 (m, 1 H, at C_7endo), 7.0 (q, 1 H, at C_3), 7.4 (q, 1 H, at C_4), and 8.22 (q, 1 H, at C_2).

***N*-Oxide of the 7-*exo*-Pentafluorobenzenesulfonate.** Treatment of 30 mg of **33**-O_3SAr in 5 mL of dichloromethane with 25 mg of 80% *m*-chloroperbenzoic acid followed by the usual workup gave 32 mg of an oil: ^{1}H NMR ($CDCl_3$) δ 2.2 (m, 4 H, at C_6 and C_9), 3.54 (m, 1 H, at C_5), 4.1 (m, 1 H, at C_8), 4.95 (m, 1 H, at C_7endo), 7.05 (overlapping m, 2 H, at C_3 and C_4), and 7.9 (q, 1 H, at C_2).

2-Chloro-6-*exo*-hydroxy-5,6,7,8-tetrahydro-5,8-methanoquinoline (34). A mixture of 112 mg of **28** and 53 mg of sodium bicarbonate in 4 mL of 50% aqueous acetone was heated overnight at 170 °C in a sealed tube. The mixture was concentrated by distilling off acetone under reduced pressure, leaving a residue, which was extracted with ether. Solvent removal and purification of the residue by Lobar-column chromatography (elution with ethyl acetate) gave 82 mg of **34** as crystals, mp 157.5–158.5 °C (dichloromethane–*n*-hexane): ^{1}H NMR ($CDCl_3$) δ 1.5–2.3 (m, 4 H, at C_7 and C_9), 2.6 (s, 1 H, OH), 3.3 (m, 2 H, bridgeheads), 4.0 (m, 1 H, at C_6endo), 7.0 (d, 1 H, at C_3), and 7.4 (d, 1 H, at C_4). Anal. Calcd for $C_{10}H_{10}NOCl$: C, 61.39; H, 5.15; N, 7.16; Cl, 18.12. Found: C, 61.46; H, 5.18; N, 7.21; Cl, 18.29.

2-Chloro-6-*exo*-pentafluorobenzenesulfonate (34-O_3SAr) was prepared from **34** as described above; mp 122–123.5 °C (ether–*n*-hexane): ^{1}H NMR ($CDCl_3$) δ 2.0–2.3 (m, 4 H, at C_7 and C_9), 3.43 (m, 1 H, at C_8), 3.72 (m, 1 H, at C_5), 4.82 (m, 1 H, at C_6endo), 7.05 (d, 1 H, at C_3), and 7.50 (d, 1 H, at C_4). Anal. Calcd for $C_{16}H_9NO_3ClF_5S$: C, 45.13; H, 2.13; N, 3.29; Cl, 8.33; F, 22.31; S, 7.53. Found: C, 45.04; H, 2.48; N, 3.27; Cl, 8.61; F, 21.86; S, 7.58.

6-*exo*-Hydroxy-2-methoxy-5,6,7,8-tetrahydro-5,8-methanoquinoline (35). A mixture of 105 mg of **31** and 51 mg of sodium bicarbonate in 6 mL of 50% aqueous acetone was warmed under reflux overnight. The workup as described above gave 90 mg of **35** as crystals, mp 109–110 °C (dichloromethane–*n*-hexane): ^{1}H NMR ($CDCl_3$) δ 1.5–2.2 (m, 4 H, at C_7 and C_9), 3.15–3.3 (m, 2 H, bridgeheads), 3.9 (overlapping 4 H, at C_6endo and OCH_3), 6.36 (d, 1 H, at C_3), and 7.30 (d, 1 H, at C_4). Anal. Calcd for $C_{11}H_{13}NO_2$: C, 69.09; H, 6.85; N, 7.33. Found: C, 69.20; H, 6.89; N, 7.30.

2-Methoxy 6-*exo*-tosylate 35-O_3SAr was prepared according to the usual manner: crystals, mp 141.5–142.5 °C (dichloromethane–*n*-hexane): ^{1}H NMR ($CDCl_3$) δ 1.7–2.2 (m, 4 H, at C_7 and C_9), 2.43 (s, 3 H, CH_3), 3.23 (m, 1 H, at C_8), 3.43 (m, 1 H, at C_5), 3.86 (s, 3 H, OCH_3), 4.5 (m, 1 H, at C_6endo), 6.36 (d, 1 H, at C_3), 7.3 (d, 1 H, at C_4), and 7.3 and 7.74 (2 sets of d, 4 H, aromatic). Anal. Calcd for $C_{18}H_{19}NO_4S$: C, 62.59; H, 5.54; N, 4.06; S, 9.28. Found: C, 62.44; H, 5.68; N, 3.96; S, 9.02.

Kinetic Materials. In the compounds synthesized for solvolyses, elementary analyses were carried out with crystalline derivatives. Oily solvolysis materials were either purified by preparative thick-layer chromatography or shown to be single compounds by thin-layer chromatography. As described in the Experimental Section of our previous work,[6] kinetic measurements showed no difference in rate constants within experimental error between analytically pure material and material purified by chromatography. Analyses by HPLC also indicated no meaningful difference between the materials.

Kinetic Measurements. Rates were determined at pH 7.5 in 50% (v/v) aqueous *tert*-butyl alcohol by using a pH stat, as described in the previous paper.[5,6]

Registry No. **9**, 5257-38-5; **10**, 58029-22-4; **11**, 110354-77-3; **12**, 110354-78-4; **13**, 110354-79-5; **14**, 110354-80-8; **15**, 110354-81-9; **16**, 110354-82-0; **17**, 110354-83-1; **17** (6-*exo*-*p*-nitrobenzenesulfonate), 110354-98-8; **17** (6-*exo*-*p*-nitrobenzenesulfonate) *N*-oxide, 110354-99-9; *endo*-**18**, 110354-84-2; *exo*-**18**, 110415-86-6; **19**, 108744-29-2; **19**-, 110354-87-5; **20**, 110354-85-3; **21**, 110354-86-4; **22**, 110415-87-7; **23**, 110354-88-6; **24**, 110354-89-7; **25**, 110354-90-0; **26**, 110354-91-1; **27**, 110354-92-2; **28**, 110354-93-3; **29**, 110354-94-4; **30**, 110354-95-5; **31**, 110354-96-6; **33**, 110354-97-7; **33** (7-*exo*-pentafluorobenzenesulfonate), 110355-00-5; **33** (7-*exo*-pentafluorobenzenesulfonate) *N*-oxide, 110355-01-6; **34**, 110355-02-7; **34** (6-*exo*-pentafluorobenzenesulfonate), 110355-03-8; **35**, 110355-04-9; **35** (6-*exo*-tosylate), 110355-05-0; $H_3COCH{=}PPh_3$, 20763-19-3; $H_2C{=}CHCH_2Br$, 106-95-6.

Sigmatropic Rearrangements of Deprotonated Allyl Phenylacetates in the Gas Phase

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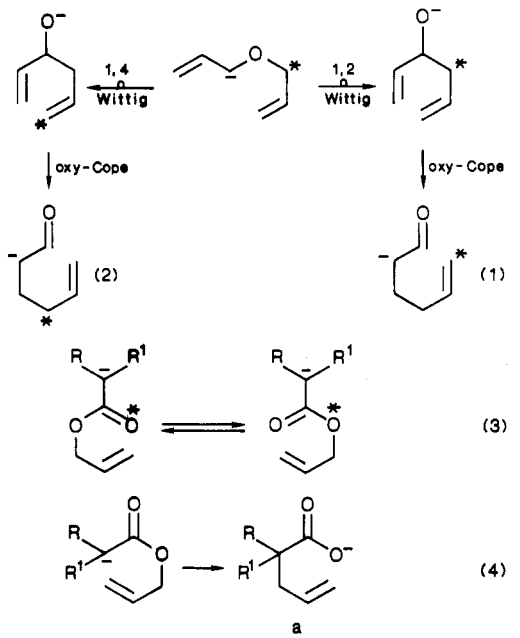
The ion $C_6H_5C^-HCO_2CH_2CH{=}CH_2$ undergoes competitive losses of C_3H_5OH and CO_2 on collisional activation. The loss of C_3H_5OH proceeds through ion complex $[C_3H_5O^-(C_6H_5CH{=}C{=}O)]$ yielding $C_6H_5C{\equiv}CO^-$ and C_3H_5OH. This reaction occurs *without* prior ester equilibration $C_6H_5C^-HC(O)O^*C_3H_5 \rightleftarrows C_6H_5C^-HC(O^*)OC_3H_5$. The elimination of CO_2 follows rearrangement $C_6H_5C^-HCO_2C_3H_5 \rightarrow C_6H_5(C_3H_5)CHCO_2^-$. The rearrangement occurs through *both* six- and four-center transition states with the six-center (Claisen) rearrangement predominating.

Introduction

Deprotonated allyl ethers can undergo Wittig, oxy-Cope, or Claisen rearrangements in the gas phase.[1,2] In particular, the diallyl ether ion rearranges first by 1,2- and 1,4-Wittig rearrangements followed by an anionic oxy-Cope rearrangement (eq 1 and 2).[2] This has led us to consider the possibility of similar six-center rearrangements of allyl esters. For example, do deprotonated allyl esters undergo oxygen equilibration by the process shown in eq 3 and the ester to carboxylate ion rearrangement shown in eq 4? Such systems have been studied in the condensed phase. Although no reaction analogous to that shown in eq 3 has been reported, neutral allyl esters undergo "oxygen equilibration" by an analogous [3,3] sigmatropic reaction

(1) Eichinger, P. C. H.; Bowie, J. H. *J. Org. Chem.* **1986**, *51*, 5078.
(2) Eichinger, P. C. H.; Bowie, J. H. *J. Chem. Soc., Perkin Trans. 2*, in press.

0022-3263/87/1952-5224$01.50/0

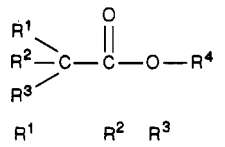


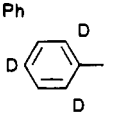
a

under forcing conditions.[3] The Claisen ester enolate rearrangement (eq 4)[4] and the related Carroll rearrangement (eq 4, R = MeCO, R^1 = H)[5] are well-known in the condensed phase. The role of solvent plays a crucial role in condensed phase reactions: gas-phase studies will indicate the fundamental reactivity of these systems in the absence of solvent. This paper investigates the possibility of reactions 3 and 4 occurring in the gas phase. Structures of product ions are probed by collisional activation studies and identified by comparison with the properties of ions of known structure.

Results and Discussion

Compounds used for this study were I–XII, $PhCH_2C(O)^{18}OCH_2CH{=}CH_2$, 2-phenyl-4-pentenoic acid, 2,2-diphenyl-4-pentenoic acid, 1,1,2-triphenylpropionic acid, 4-phenylbut-1-ene-*1,1-*d_2 and 4-(phenyl-d_5)but-1-ene. Collisional activation (CA) mass spectra are recorded in Figures 1 and 2 and Table I. Charge reversal (CR) mass spectra are recorded in Table II. Experimental details are outlined in the Experimental Section.



	R^1	R^2	R^3	R^4
I	Ph	H	H	Me
II	Ph	D	D	Me
III	Ph	H	H	Et
IV	Ph	H	H	Pr
V	Ph	H	H	allyl
VI	Ph	D	D	allyl
VII	Ph	H	H	$CD_2CH{=}CH_2$
VIII		H	H	allyl
IX	Ph	Ph	H	allyl
X	Ph	Ph	H	$CD_2CH{=}CH_2$
XI	Ph	H	H	CH_2Ph
XII	Ph	Ph	H	CH_2Ph

(3) Lewis, E. S.; Hill, J. T.; Newman, E. R. *J. Am. Chem. Soc.* **1968**, *90*, 662. Barton, D. H. R.; Magnus, P. D.; Pearson, M. J. *J. Chem. Soc., Chem. Commun.* **1969**, 550.

(4) Brannock, K. C.; Pridgen, H. S.; Thompson, B. *J. Org. Chem.* **1960**, *25*, 1815. Frater, A. *Helv. Chim. Acta* **1975**, *58*, 442. Ireland, R. E.; Mueller, R. H.; Willard, A. K. *J. Am. Chem. Soc.* **1976**, *98*, 2868.

(5) Carroll, M. F. *J. Chem. Soc.* **1940**, 1266. Kimel, W.; Cope, A. C. *J. Am. Chem. Soc.* **1943**, *65*, 1992 and references cited therein.

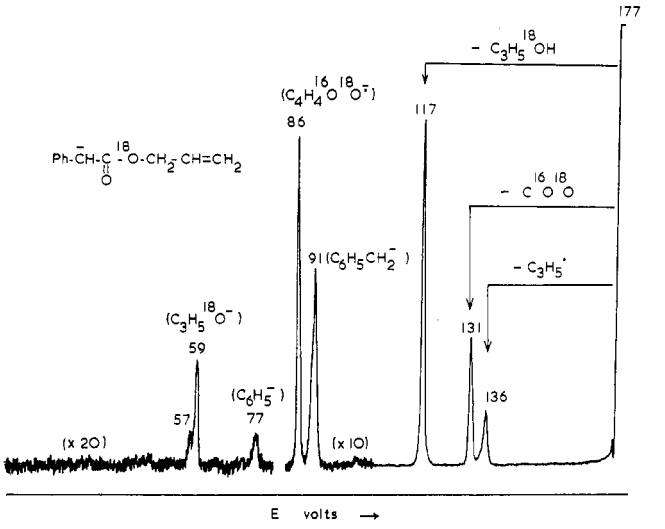


Figure 1. CA mass spectrum of $PhC^-HC(O)^{18}OCH_2CH{=}CH_2$. For experimental conditions, see Experimental Section. Applying a potential of +2000 V to the collision cell indicates the following collision induced: unimolecular ratio (m/z (CI:u) [loss]), 136 (60:40) [$C_3H_5^{\cdot}$], 131 (10:90) [$C^{16}O^{18}O$], 117 (45:55) [$C_3H_5{}^{18}O$], 91 (80:20) [$C_4H_4{}^{16}O^{18}O$], 86 (40:60) [$C_7H_7^{\cdot}$], 77 (90:10) [$C_5H_6{}^{16}O^{18}O$], and 59 (70:30) [C_3H_6O].

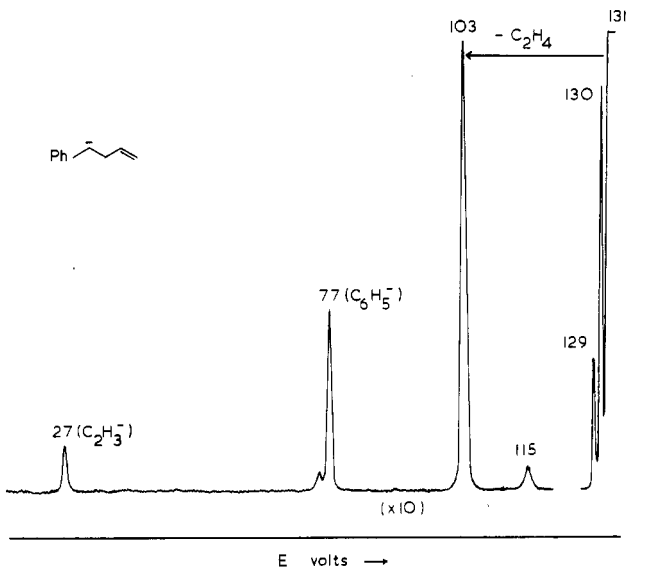
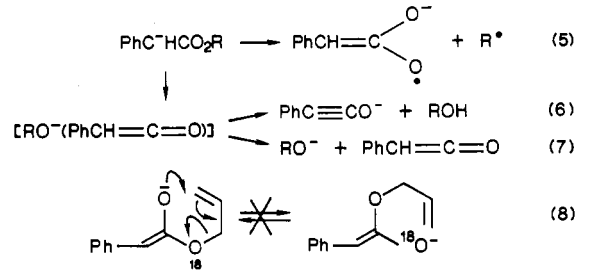


Figure 2. CA mass spectrum of $PhC^-HCH_2CH{=}CH_2$ (formed in the ion source by decarboxylation of $Ph(CH_2{=}CHCH_2)CHCO_2^-$).

The fragmentations of enolate ions of alkyl phenylacetates are recorded in Table I. They are characteristic of simple esters[6-8] and are summarized in eq 5 and 6. Loss



(6) Hunt, D. F.; Giordani, A. B.; Shabanowitz, J.; Rhodes, G. *J. Org. Chem.* **1982**, *47*, 738.

(7) Froelicher, S. W.; Lee, R. E.; Squires, R. R.; Freiser, B. S. *Org. Mass Spectrom.* **1985**, *20*, 4.

Table I. CA Mass Spectra of Enolate Ions of Substituted Phenylacetates PhC^-HCO_2R

parent ion	loss				formation										
	H·	D·	R·	ROH	ROD	CO_2	$PhCH_2^-$	PhCHD⁻	$C_6H_2D_3C^-$	Ph_2CH^-	Ph_2CD^-	$C_4H_4O_2^{\cdot-}$	$C_4H_3DO_2^{\cdot-}$	$C_3H_5O^-$	$C_3H_4DO^-$	$C_3H_3O^-$	$C_3H_2DO^-$
PhC^-HCO_2Me	15		7	100													
PhC^-DCO_2Me	13		5		100												
PhC^-HCO_2Et	11		12	100													
PhC^-HCO_2Pr	18		14	100													
PhC^-HCO_2 allyl[a]	10		17	100		66	5					8		3		1	
PhC^-DCO_2 allyl	11		15		100	58		6				9		3		1	
$PhC^-HCO_2CD_2CH{=}CH_2$	16		20	100		81		4					8		3		1
(Ph-2,4,6-d_3)C^-HCO_2 allyl	8	4	19	100		64			5			8		2		0.6	
$Ph_2C^-CO_2$ allyl	21		16			100				35[b]					2		0.6
$Ph_2C^-CO_2CD_2CH{=}CH_2$	19		9			100					23[c]						
$PhC^-HCO_2CH_2Ph$	5		33	100		8	4								2		
$Ph_2C^-CO_2CH_2Ph$	d		11	15		55[e]	2		9								

[a] Width of peaks at half-height, m/z (loss/formation) [volts ±0.2]; 134 (–$C_3H_5^{\cdot}$) [58.2], 131 (–CO_2) [41.1], 117 (–C_3H_5OH) [48.5], 91 ($PhCH_2^-$) [48.8], 84 ($C_4H_4O_2^{\cdot-}$) [40.8], and 57 ($C_3H_5O^-$) [45.2]. [b] The spectrum also contains a peak of 40% abundance corresponding to $C_{13}H_9^-$ (i.e., $Ph_2CH^- - H_2$). [c] The spectrum also contains peaks corresponding to $C_{13}H_8D^-$ (28%) and $C_{13}H_9^-$ (5%). [d] Loss of H· not resolved; in this case loss of H_2 = 100%. [e] Applying a potential of +2000 V to the collision cell shows the loss of CO_2 to be 85% unimolecular and 15% collision induced.

Table II. Charge Reversal Mass Spectra of $Ph_2(CH_2{=}CHCH_2)C^-$ and m/z 207 from $Ph_2C^-CO_2CH_2CH{=}CH_2$

m/z (relative abundance of ion from $Ph_2(CH_2{=}CHCH_2)C^-$, relative abundance of ion from decomposition of m/z 207]
207 (6, 5), 206 (16, 18), 205 (24, 23), 203 (28, 27), 202 (28, 25), 191 (34, 31), 189 (22, 23), 177 (55, 52), 165 (100, 100), 152 (41, 43), 151 (38, 41), 139 (24, 24), 128 (71, 68), 127 (68, 67), 115 (50, 52), 103 (22, 20), 91 (57, 56), 89 (16, 15), 77 (44, 41), 65 (8, 8), 63 (24, 23), 51 (24, 25), 41 (2, 2), 39 (9, 9), 27 (2, 2)

of CO_2 is not observed in these spectra, so there is no indication of migration of R to the carbanion center in these cases. The spectra of the $(M - H^+)^-$ ion of allyl phenylacetate and of its deuterium-labeled derivatives (VI–VIII) are listed in Table I, while that of $PhC^-HC(O)^{18}OCH_2CH{=}CH_2$ is shown in Figure 1. Major fragmentations of the allyl ester ion are the loss of $C_3H_5^{\cdot}$ (eq 5) and allyl alcohol (eq 6), together with the formation of the allyloxy anion (eq 7). The spectrum (Figure 1) of the ^{18}O derivative shows *specific* loss of $CH_2{=}CHCH_2{}^{18}OH$.[9,10] Thus *the allyl ester rearrangement shown in eq 8 does not occur upon collisional activation.*

In contrast, allyl rearrangement to the carbanion site does occur as evidenced by the pronounced losses of carbon dioxide from $PhC^-HCO_2CH_2CH{=}CH_2$ (Table 1, Figure 1) and $Ph_2C^-CO_2C_3H_5$ (Table I).[11] The reactions plausibly proceed through the intermediacy of carboxylate ions a (eq 4, R = Ph, R^1 = H and Ph, respectively) since the losses of CO_2 from "$PhC^-HCO_2C_3H_5$" and authentic $Ph(C_3H_5)CHCO_2^-$ (formed by deprotonation of the corresponding carboxylic acid) both produce Gaussian peaks with widths at half height of 41.1 ± 0.2 V. The corresponding peak widths for losses of CO_2 from $Ph_2C^-CO_2C_3H_5$ and $Ph_2(C_3H_5)CCO_2^-$ are 46.6 ± 0.2 V.[12] The product ions formed by loss of CO_2 are likely to correspond to $Ph(R)C^-CH_2CH{=}CH_2$ (R = H or Ph) since in the latter case (R

(8) Hayes, R. N.; Bowie, J. H. *Org. Mass Spectrom.* **1986**, *21*, 425. Hayes, R. N.; Bowie, J. H. *J. Chem. Soc., Perkin Trans. 2* **1986**, 1827.

(9) The data shown in the legend to Figure 1 indicate that the elimination of $C_3H_5{}^{18}OH$ has an appreciable collision-induced component (55% under the reaction conditions used). Even so, 45% of the loss of $C_3H_5{}^{18}OH$ occurs before the parent enolate ions reach the collision cell. Thus deprotonation of the ester must yield some enolate ions which have sufficient internal energy to allow unimolecular elimination of $C_3H_5{}^{18}OH$.

(10) Figure 1 shows a peak at m/z 59 ($C_3H_5{}^{18}O^-$) together with a smaller peak at m/z 57. The corresponding CA mass spectrum of $PhC^-HCO_2CH_2CH{=}CH_2$ (see Table I) shows peaks at m/z 57 ($C_3H_5O^-$) and 55 ($C_3H_3O^-$) in the ratio 3:1. The peak at m/z 55 presumably occurs by the process

$$CH_2{=}CHCH_2O^- \longrightarrow [H^-(CH_2{=}CHCHO)] \longrightarrow CH_2{=}C{=}C(O^-)H + H_2$$

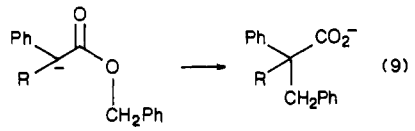
(cf.: Klass, G.; Sheldon, J. C.; Bowie, J. H. *J. Chem. Soc., Perkin Trans. 2* **1983**, 1337). Thus the peak at m/z 57 in Figure 1 corresponds to $C_3H_3{}^{18}O^-$. A small contribution of $C_3H_5{}^{16}O^-$ to m/z 57 cannot be excluded on the experimental evidence. However the loss of $C_3H_5{}^{18}OH$ is *specific* as seen in Figure 1: in addition, a B/E linked scan confirms there is no loss of $C_3H_5{}^{16}OH$.

(11) A reviewer has asked whether the allyl esters could pyrolyze in the inlet systems of the ZAB 2HF instrument, i.e., could the rearrangement be a neutral rearrangement? (Liquids were introduced through the all-glass septum inlet system at 100 °C, solids through the direct probe at 120 °C). $PhCH_2CO_2CH_2CH{=}CH_2$ was heated at 160 °C at atmospheric pressure under nitrogen) for 6 h. Thin-layer chromatography and gas chromatography showed unchanged starting material; no decomposition products were noted.

(12) This is a standard procedure used to indicate whether two decomposing ions have the same structure (and energy distribution). The width of the peak is a function of the kinetic energy release occurring during the decomposition. See: Cooks, R. G.; Beynon, J. H.; Caprioli, R. M.; Lester, G. R. *Metastable Ions*; Elsevier: Amsterdam, 1973; pp 104–122.

= Ph) the charge reversal (positive ion) spectrum[13] is very similar to that of the ion formed by decarboxylation of $Ph_2(C_3H_5)CCO_2^-$ (see Table II). The data recorded in the legend to Figure 1 indicates that 90% of the loss of CO_2 occurs *before* the decomposing ion reaches the collision cell, with only 10% of the overall loss being collision induced. Thus, *most of the decomposing carboxylate anions (a, eq 4) are formed in the ion source* and do not require collisional activation.[14]

Although the decarboxylation of the deprotonated allyl esters may occur following Claisen rearrangement (eq 4), we must also consider the possibility of a 1,4-rearrangement. This type of rearrangement is illustrated by the spectra (Table I) of the enolates from the benzyl esters XII and XIII, in which carbon dioxide loss is also noted. Claisen rearrangement cannot occur in these cases, the probable mechanism is shown in eq 9. The following



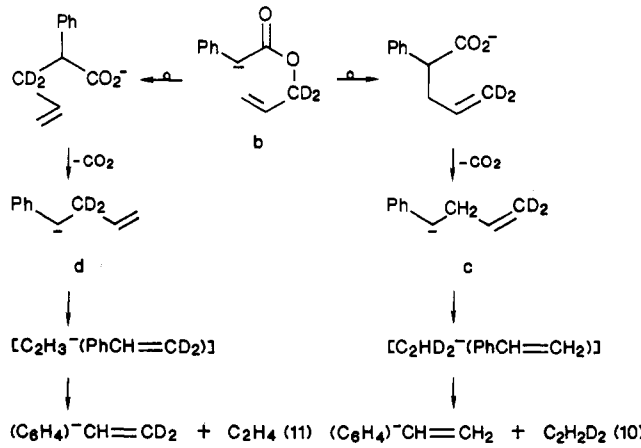
(9)

evidence supports the operation of 1,4 rearrangements in these cases. (i) The losses of CO_2 from "$Ph_2C^-CCO_2CH_2Ph$" and $Ph_2(PhCH_2)CCO_2^-$ (formed by deprotonation of the corresponding carboxylic acid) both produce a Gaussian peak with a width at half-height of 39.6 ± 0.3 V; thus it is likely that the structures of both decomposing ions are the same.[12] (ii) The product ion produced by loss of CO_2 from "$Ph_2C^-CO_2CH_2Ph$" is $Ph_2(PhCH_2)C^-$, since its CA mass spectrum is identical with that of authentic $Ph_2(PhCH_2)C^-$ formed by decarboxylation of $Ph_2(PhCH_2)CCO_2^-$ in the ion source.[15]

Thus we must consider the two possibilities shown in Scheme I for the D_2, ion b, viz., *since ester equilibration does not occur*, the six-center Claisen process proceeds via route b → c and four-center process by route b → d. It should be possible to differentiate between these two processes since c and d should fragment differently. A major fragmentation of $PhC^-HCH_2CH{=}CH_2$ is loss of ethene (see Figure 2), thus c should eliminate $C_2H_2D_2$ (eq 10, Scheme I) whereas d should lose C_2H_4 (eq 11).[16] We confirm that c and d should fragment in this manner, since independently prepared ions $C_6D_5C^-HCH_2CH{=}CH_2$ and $PhC^-HCH_2CH{=}CD_2$ fragment principally by the processes, $C_6D_5C^-HCH_2CH{=}CH_2 \rightarrow (C_6D_4)^-CH{=}CH_2 + C_2H_3D$ and $PhC^-HCH_2CH{=}CD_2 \rightarrow (C_6H_4)^-CH{=}CH_2 + C_2H_2D_2$.[17] *Thus the ratio of the losses of $C_2H_2D_2$ and C_2H_4 from the ion(s) formed by the loss(es) of CO_2 from b (Scheme I) will indicate the Claisen (b → c) and 1,4 (b → d) rearrangement ratio.*

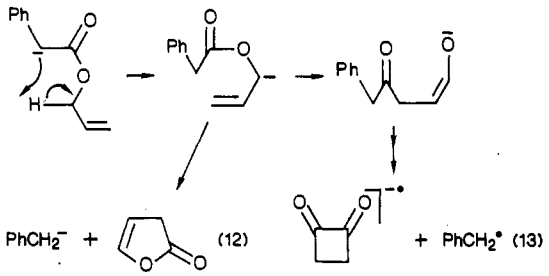
The experiment to be performed requires the determination of a CA mass spectrum of an ion formed in the

Scheme I



original CA mass spectrum; i.e., it requires an MS/MS/MS capability. This facility is not available with the ZAB 2HF instrument. The following experiments were carried out with the Kratos TA 50 (EBE) instrument at the University of Nebraska—Lincoln. The ions at m/z 135 formed by decarboxylation of b (Scheme I) showed losses of $C_2H_2D_2$ and C_2H_4 in the ratio 60:40. The ions at m/z 209, formed by the analogous loss of CO_2 from $Ph_2C^-CO_2CD_2CH{=}CH_2$ showed losses of $C_2H_2D_2$ and C_2H_4 in the ratio 90:10. *Thus both mechanisms operate, with the Claisen rearrangement being the more important in both cases.*

Finally, there are two processes from $PhC^-HCO_2CH_2CH{=}CH_2$ which occur following transfer of an allylic proton to the benzylic position. First, the formation of the benzyl anion which we represent in eq 12 (a similar



reaction forms Ph_2CH^- from $Ph_2C^-CO_2CH_2CH{=}CH_2$—see Table I), and secondly, an ion $C_4H_4O_2^{\bullet-}$ which we suggest is the α-dicarbonyl radical anion shown in eq 13.[18]

In conclusion, we have answered the questions posed in the introduction, i.e., i) The [3,3] sigmatropic enolate ester equilibration $PhC^-HC(O)^{18}OCH_2CH{=}CH_2 \rightleftarrows PhC^-HC(^{18}O)OCH_2CH{=}CH_2$ does not occur upon collisional activation in the gas phase. (ii) Ions $PhC^-(R)CO_2CH_2CH{=}CH_2$ (R = H and Ph) undergo facile rearrangement to $Ph(CH_2{=}CHCH_2)(R)CCO_2^-$ through both six- and four-centered transition states. In contrast, $Ph_2C^-CO_2CH_2Ph$

(13) Firing a polyatomic negative ion through a collision cell (containing, say, helium) can effect charge stripping of the negative ion to a decomposing positive ion. This produces a charge reversal (CR) (positive ion) spectrum. If two negative ions give identical CR mass spectra, there is a probability that the original negative ions had the same structure. See, e.g.: Bowie, J. H.; Blumenthal, T. *J. Am. Chem. Soc.* **1975**, *97*, 2959. Howe, I.; Bowie, J. H.; Szulekjo, J. E.; Beynon, J. H. *Int. J. Mass Spectrom. Ion Phys.* **1980**, *34*, 99.

(14) No clear statement can be made concerning those decompositions which are collision induced. Collisional activation could convert some nondecomposing enolate anions into decomposing carboxylate anions and/or collisionally activate carboxylate anions which initially had insufficient energy to effect decomposition.

(15) The CA mass spectrum of $Ph_2(PhCH_2)C^-$ is as follows (m/z (loss) [relative intensity]): 256 ($H^{\bullet}$) [100], 255 (H_2) [28], 243 (CH_2) [1], 179 (C_6H_6) [10], 165 (C_7H_9) [1], 153 (C_8H_8) [3], and 77 ($C_{14}H_{12}$) [9].

(16) It has been reported that substituted benzyl anions fragment through ion complexes. Currie, G. J.: Bowie, J. H.; Massy-Westropp, R. A.; Adams, G. W. *J. Chem. Soc., Perkin Trans. 2*, in press. The other fragmentation of ion complex $[C_2H_3^-(PhCH{=}CH_2)]$ is formation of $C_2H_3^-$ (see Figure 2).

(17) The CA mass spectra of $C_6D_5C^-HCH_2CH{=}CH_2$ and $PhC^-HCH_2CH{=}CD_2$ are as follows (m/z (loss) [relative intensity]. $C_6D_5C^-HCH_2CH{=}CH_2$; 134 ($D^{\bullet}$, H_2) [100], 133 (HD) [24], 107 (C_2H_3D) [2], 82 (C_4H_6) [4], and 27 ($C_3H_3D_5$) [1]. $PhC^-HCH_2CH{=}CD_2$: 132 ($H^{\bullet}$) [100], 131 (H_2, $D^{\bullet}$) [28], 130 (HD) [8], 103 ($C_2H_2D_2$) [8], 77 ($C_4H_4D_2$) [5], and 29 (C_3H_3) [1].

(18) The electron affinity of cyclobutane-1,2-dione is not known, but it should certainly not be less than 1.5 eV. The cyclobutane-1,2-dione anion radical should form in preference to the benzyl anion (the electron affinity of $PhCH_2^{\bullet}$ is 0.88 eV: Drzaic, P. S.; Brauman, J. I. *J. Am. Chem. Soc.* **1984**, *106*, 3443).

rearranges to $Ph_2(PhCH_2)CCO_2^-$ through a four-center state.

Experimental Section

CA mass spectra were measured with a Vacuum Generators ZAB 2HF mass spectrometer operating in the negative chemical ionization mode. All slits were fully open to obtain maximum sensitivity and to minimize energy resolution effects.[19] The chemical ionization slit was used in the ion source: ionizing energy 70 eV (tungsten filament), trap current 100 μA, ion source temperature 150 °C, accelerating voltage 8 kV. Liquids were introduced through the septum inlet at 100 °C, solids through the direct probe at 120 °C. Carbanions were generated by H^+ abstraction by HO^- (or H^- or $O^{\bullet-}$) (compounds I, III, IV, IX, XI, XII) or D^+ abstraction by DO^- (or D^- or $O^{\bullet-}$) (compounds II, VI–VIII, X). Reactant negative ions were generated from either H_2O or D_2O by 70-eV electrons.[20] The indicated source pressure (of H_2O or D_2O) was typically 5×10^{-4} Torr. The substrate pressure was typically 5×10^{-7} Torr. The *estimated* total pressure within the source is 10^{-1} Torr. The pressure of He in the second collision cell was 2×10^{-7} Torr, measured by an ion gauge situated between the electric sector and the second collision cell. This produced a decrease in the main beam signal of ca. 10% and thus corresponds to essentially single collision conditions.

The MS/MS/MS spectra were measured with a Kratos TA 50 (EBE) instrument, operating at 70 eV in the CI mode. The measured pressure of water (plus sample) in the source was 2×10^{-5} Torr. Helium collision gas was used in both collision cells (measured pressure 2×10^{-7} Torr), and the decrease in main beam was 10% in each case.

All unlabeled compounds were prepared by reported procedures; viz., I,[21] III,[22] IV,[22] V,[23] IX,[24] XI,[25] XII,[26] 2-phenyl-4-pentenoic acid,[27] 2,2-diphenyl-4-pentenoic acid,[28] and 1,1,2-triphenylpropionic acid.[29]

Labeled compounds VI, VII, VIII, and $PhCH_2C(O)^{18}OCH_2CH{=}CH_2$ were made by the following general method.

The appropriate allyl alcohol (102 mg) in anhydrous chloroform (0.70 mL) was added dropwise to a solution of the appropriate phenylacetyl chloride (270 mg) in anhydrous pyridine (180 mg) and chloroform (1.3 mL) maintained at 0 °C. The mixture was allowed to stir at 10 °C for 12 h, dichloromethane (2.5 mL) was added, and the organic phase was washed with aqueous ammonium chloride (saturated, 2 × 2 mL), aqueous sodium hydrogen carbonate (saturated, 2 × 2 mL), and aqueous sodium chloride (saturated, 2 mL). The solvent was removed in vacuo, and distillation gave the appropriate ester in (on average) 90% overall yield, bp 101–102 °C (2 mmHg). Compounds II and X were prepared by the same general procedure using phenylacetyl chloride/methanol and diphenylacetyl chloride/allyl-*1,1*-d_2 alcohol, respectively.

Allyl-*1,1*-d_2 alcohol was prepared by the method of Bartlett.[30]

Allyl Alcohol-^{18}O. Calcium hydride (1.26 g) was added cautiously to water-^{18}O (1.5 mL, ^{18}O = 20.9 atom %) in an ampule until evolution of hydrogen ceased. Allyl iodide (1.63 g) was added, the ampule sealed, the mixture heated at 110 °C for 6 days and cooled to 15 °C, the ampule broken, and dry hydrogen chloride bubbled into the reaction mixture until the pH was 7. Distillation gave allyl alcohol-^{18}O as a colorless liquid (bp 96–98 °C); yield 0.46 g (79%).

Phenylacetyl chloride-*2,2*-d_2 (d_2 = 99%) and (phenyl-*2,4,6*-d_3)acetyl chloride (d_3 > 98%) were made from the appropriately labeled benzyl chlorides[1] by carbonation of the Grignard reagent,[31] followed by treatment with phosphorus pentachloride.[32]

4-Phenylbut-1-ene-*1,1*-d_2. The Wittig reaction[33] between 3-phenylpropanal and triphenylphosphonium trideuteriomethyl iodide gave 4-phenylbut-1-ene-*1,1*-d_2 in 47% yield (d_2 = 99%).

4-(Phenyl-*1,2,3,4,5*-d_5)but-1-ene. The coupling reaction[34] between 4-iodobut-1-ene[35] and lithium di(phenyl-d_5)cuprate[34] at 0 °C gave 4-(phenyl-*1,2,3,4,5*-d_5)but-1-ene in 78% yield (d_5 = 99%).

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Registry No. I, 101-41-7; II, 50848-70-9; III, 101-97-3; IV, 4606-15-9; V, 1797-74-6; VI, 61233-42-9; VII, 110374-96-4; VIII, 110374-97-5; IX, 88017-70-3; X, 110374-98-6; XI, 102-16-9; XII, 37537-23-8; $CH_2{=}CHCH_2CH(Ph)CO_2H$, 1575-70-8; $CH_2{=}CHCH_2C(Ph)_2CO_2H$, 6966-03-6; $PhCH_2C(Ph)_2CO_2H$, 2902-61-6; $CD_2{=}CH(CH_2)_2Ph$, 110374-99-7; $CH_2{=}CH(CH_2)_2Ph$, 768-56-9; $PhCH_2C(O)^{18}OCH_2CH{=}CH_2$, 110375-00-3; $CH_2{=}CHCH_2{}^{18}OH$, 25023-06-7; $PhC(D)_2Cl$, 33712-34-4; $2,4,6\text{-}D_3C_6H_2CH_2Cl$, 91588-64-6; $PhC(D)_2COCl$, 59211-45-9; $2,4,6\text{-}D_3C_6H_2COCl$, 110375-01-4; $CH_2{=}CHC(D)_2OH$, 10475-51-1; $Ph_3PCD_3{}^{+\bullet}I^-$, 1560-56-1; $CH_2{=}CH(CH_2)_2I$, 7766-51-0; $PhCH^-CO_2Me$, 110375-03-6; $PhCD^-CO_2Me$, 110375-04-7; $PhCH^-CO_2Et$, 75748-20-8; $PhCH^-CO_2Pr$, 110375-05-8; $PhCH^-COOCH_2CH{=}CH_2$, 110375-06-9; $PhCD^-COOCH_2CH{=}CH_2$, 110375-07-0; $PhCH^-COOCD_2CH{=}CH_2$, 110375-08-1; $2,4,6\text{-}D_3C_6H_2CH^-COOCH_2CH{=}CH_2$, 110375-09-2; $Ph_2C^-CO_2CH_2CH{=}CH_2$, 110375-10-5; $Ph_2C^-CO_2CD_2CH{=}CH_2$, 110375-11-6; $PhCH^-CO_2CH_2Ph$, 110375-12-7; $Ph_2C^-CO_2CH_2Ph$, 110375-13-8; $Ph_2C^-CH_2CH{=}CH_2$, 110375-14-9; $CH_2{=}CHCH_2I$, 556-56-9; $CH_2{=}CHCH_2OH$, 107-18-6; $PhCH_2COCl$, 103-80-0; $(Ph)_2CHCOCl$, 1871-76-7; $Ph(CH_2)_2CHO$, 104-53-0; lithium di(phenyl-d_5)cuprate, 110375-02-5.

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