

Primary and Secondary Kinetic Isotope Effects in the Decomposition of a Tertiary Alkoxide

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Kinetic isotope effects have been determined for the elimination of toluene from the alkoxide of 1,2,3-triphenylpropan-2-ol (**1a**). In DMSO, the rate measurements on **1a** and [1,1,3,3-²H₄]1,2,3-triphenylpropanol (**1b**) at 30 °C give $k_{\text{H}_4}/k_{\text{C}_4} = 1.68$. For the enolate products of reactions of [1,3-²H₂]- and [1,1-²H₂]-1,2,3-triphenylpropanol (**1c** and **1d**), isolated as enol ethers, the ratio of deuterated to undeuterated products was 2.67 and 1.37, respectively. The ratio of undeuterated to deuterated toluenes from **1d** was 1.46. In the reaction of [1-¹³C]-1,2,3-triphenylpropanol (**1e**) the ratio of ¹³C-labelled product to unlabelled was 1.064. The data are shown to be consistent with rate-limiting expulsion of a benzyl anion from the alkoxide, followed by fast proton transfers involving a solvent molecule to yield the observed products. The negative chemical ionization spectrum of **1a** shows ions corresponding to deprotonated alcohol and the enolate of 1,2-diphenylethanone. The ratios of deuterated to undeuterated enolates in the *B/E* linked spectra of **1c** and **1d** were 2.47 and 0.72, respectively, and the ratio of ¹³C-enolate to unlabelled enolate in the fragmentation of **1e** was 1.083. These data are rationalized in terms of an ionic fragmentation to an ion-dipole complex of 1,2-diphenylethanone and benzyl anion followed by a proton transfer which is at least partially rate limiting within the complex to yield the enolate.

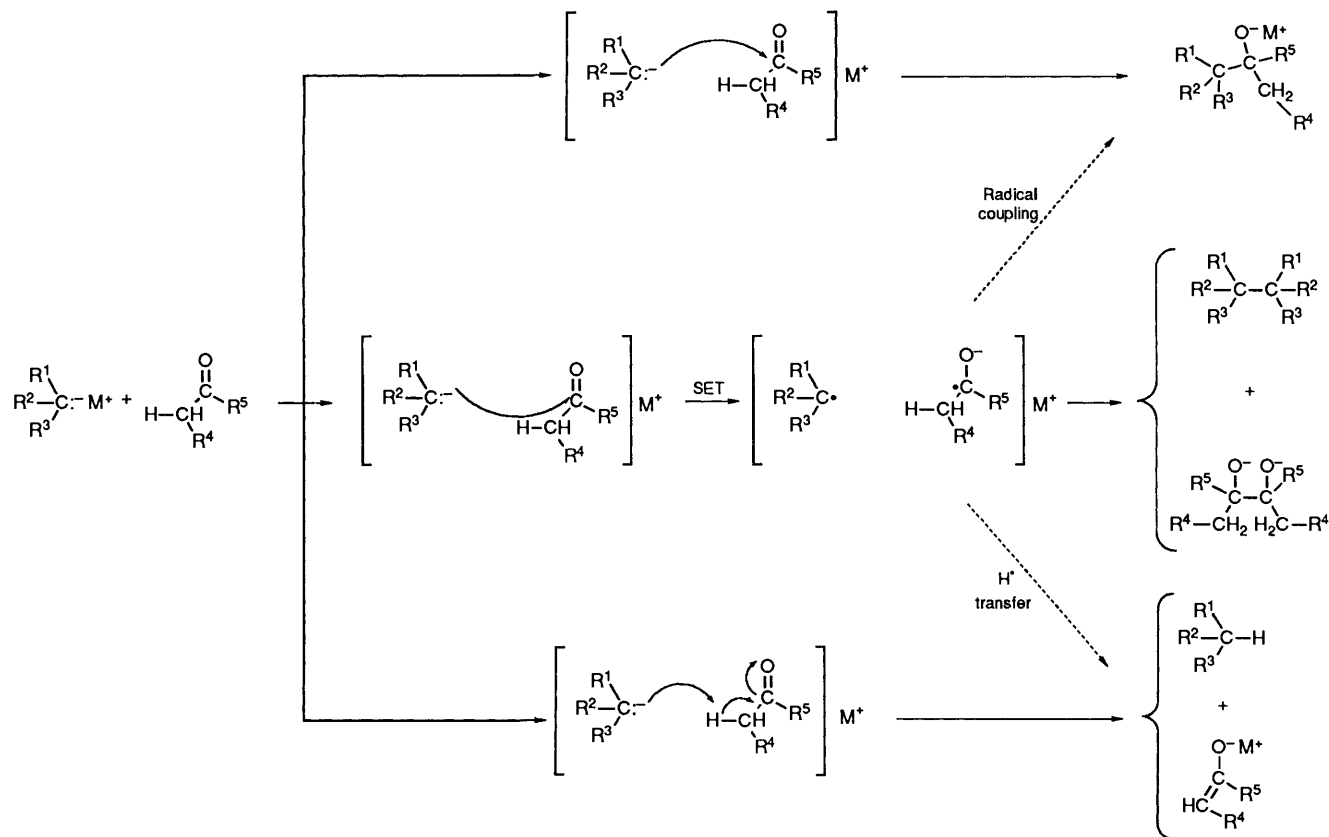
Formal additions of carbanions derived from weak carbon acids ($\text{p}K_{\text{a}} > 40$) to ketonic carbonyl groups are the basis of many reactions of synthetic and biological importance. A broad understanding of their mechanism has allowed the development of useful rules for the prediction of yields and stereochemical course in particular cases, but questions remain as to the details of the major bonding changes and as to the nature of the ketone-carbanion complex which must precede carbon-carbon bond formation. Experimental investigation of this complex from the carbanion + carbonyl side of the reaction has many difficulties, not least of which is identification of the reactive carbanionic reagent amongst a host equilibrating associated forms of organometallic reagents. There are indications, however, that alkoxide fragmentations might provide a more useful entry to high energy intermediates on the reaction pathway. Tertiary alkoxides decompose by formal elimination of one of the hydrocarbon groups attached to the alcohol carbon, yielding hydrocarbon and either a ketone or its enolate anion.¹ Fragmentations occur in both solution and gas phases,² and, in many but not all cases^{1,3} occur by collapse of alkoxide to ketone and carbanion followed by proton transfers, either within the ketone-carbanion complex, or involving solvent. Where there is charge delocalization in the carbanion or strain is relieved,⁴ these reactions proceed rapidly at near ambient temperatures in solvents such as DMSO. They thus provide access to the carbonyl-carbanion complex at the reaction branch point leading (from the addition point of view) either to alkoxide by carbon-carbon bonding or to enolate + hydrocarbon by proton transfers as shown in Scheme 1. Homolytic cleavages to alkyl radical and ketyl may also occur. These may lead to the same products by hydrogen atom transfer in the radical-radical anion pair, but additional coupling products are to be expected when the radicals have sufficient lifetime to escape a solvent cage although Walling has shown that high yields of normal products (in the addition sense) are possible without assuming significant reaction within the solvent cage.⁵

We have recently examined the reactions of the alkali metal salts of 1,2,3-triphenylpropanol (**1**). In DMSO solution, these react at convenient rates ($4000 \text{ s} > t_{\frac{1}{2}} > 2 \text{ s}$ at 25 °C), yielding toluene and the enolate of 1,2-diphenylethanone,⁶ isolated as

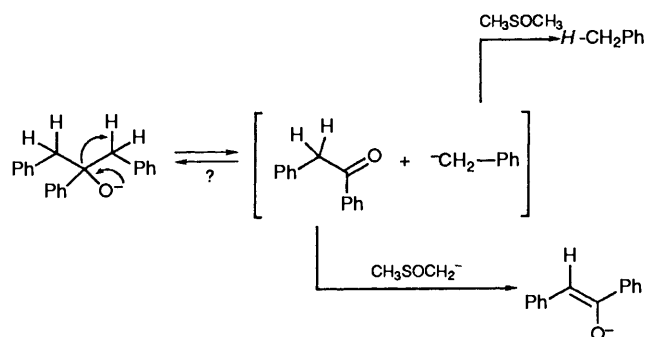
the ketone after aqueous quenching. Additional products such as 1,2-diphenylethane, or 1,2,3,4-tetraphenylbutane-2,3-diol are not found, and both the rate and product data have been interpreted in terms of the general mechanistic scheme outlined above with collapse of alkoxide yielding a transient benzyl anion and 1,2-diphenylethanone. Proton transfers involving solvent then yield the observed products, but it has not yet been established which event, carbon-carbon bond cleavage, proton transfer, or possibly solvent insertion into the initial complex, is rate limiting.

An initial bond homolysis to a benzyl radical-radical anion-pair followed by electron and hydrogen atom transfers are certainly not excluded by the rate and product data, but the description of the reaction as anionic cleavage and proton transfer is supported in the absence of any line broadening or unusual signal intensities indicative of CIDNP in proton NMR spectroscopic monitoring of the reaction. The spectrum of the alkoxide (sodium salt in DMSO) evolves smoothly to that of the enolate and toluene. Additionally, it is possible to make good estimates of the relative gas phase energies of alkoxide, benzyl anion and radical, ketone and ketyl from available thermochemical data,⁷ and gas phase proton⁸ and electron affinity measurements.⁹ The combined results are shown in Fig. 1. Relative to the alkoxide, the energy sink is the enolate and hydrocarbon. Of the possible cleavage modes, that leading to a separate benzyl anion and ketone is favoured by 15 kcal mol⁻¹ over that yielding a benzyl radical and ketyl. Between alkoxide and these extremes lies the complex of carbanion and ketone (or radical-ketyl pair) stabilized relative to the separate species by an ion-dipole interaction. A quantitative estimate of this stabilization is not easy to obtain; most experimental measurements have been on cationic rather than anionic complexes. Estimates from average dipole orientation theory¹⁰ and experimental data on dimeric aromatic cluster ions bound only by non-specific interactions yield values between 10 and 15 kcal mol⁻¹. With the high dipole moment of the carbonyl group, the interaction in the benzyl anion-ketone complex could well be larger, in which case, the initial bond cleavage in the alkoxide might be thermoneutral or even slightly exothermic.

In solution, energies will reflect differential solvation of the

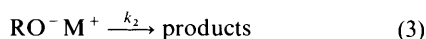
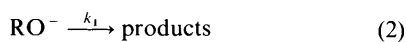
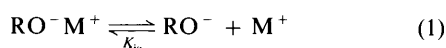


Scheme 1 Alkoxide fragmentations and carbanion-carbonyl combinations

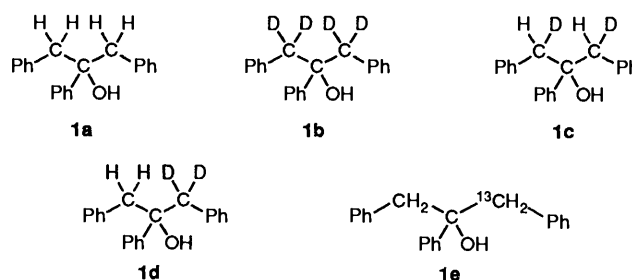


Scheme 2 Fragmentation of 1,2,3-triphenylpropoxide in DMSO

anionic species, but in aprotic dipolar solvents this is unlikely to be enough to alter their ordering of stabilities.¹¹ Association with cations must also be considered, especially for the alkoxides with their localized charge. DMSO solutions of alkali metal salts are indeed highly associated¹² with, for example, $K_{ip} = 10^6$ for sodium *tert*-butoxide. However, the dependence of rates of product formation from salts of **1** (RO^-M^+) on the nature and concentration of the cation (M^+) is fully consistent with the reaction scheme⁶ outlined in reactions (1)–(3), where the ion-paired alkoxide, RO^-M^+ , dissociates prior to fragmentation, *i.e.*, $k_1 \gg k_2$. Under these circumstances, the gas-phase energetics may be a useful guide to behaviour of the alkoxides in the solution reactions, at least in aprotic media.



We now describe experiments with isotopically labelled derivatives of **1** designed to probe further the nature and timing of the bonding changes in the formation of hydrocarbon and enolate. Specifically, we have prepared the deuteriated compounds **1b**, **1c** and **1d**, and the ¹³C-isotopomer **1e** and examined the reactions of their alkoxides in both solution and gas phases.¹³



Results

Preparation and Characterization of the Alcohols.—Deuteriated precursors, 2,2-dideuterio-1,2-diphenylethanone and 1,1,3,3-tetradeuterio-1,3-diphenylpropanone were prepared by base-catalysed exchange of enolizable protons in deuterium oxide. Reaction with benzylmagnesium chloride or phenylmagnesium chloride, respectively, then provided the alcohols **1d** and **1b** without complication. ¹H NMR spectroscopy using integrations over the AB-quartet from diastereotopic benzylic hydrogens at δ 3.25 indicated high deuterium incorporation and IR spectra showed the expected bands at ν_{max} 2175 cm^{-1} associated with C-D stretches. Conventional positive ion mass spectrometry with electron impact or chemical ionization did not yield ions suitable for accurate estimation of deuterium incorporation. For the EI spectra, no molecular ion was

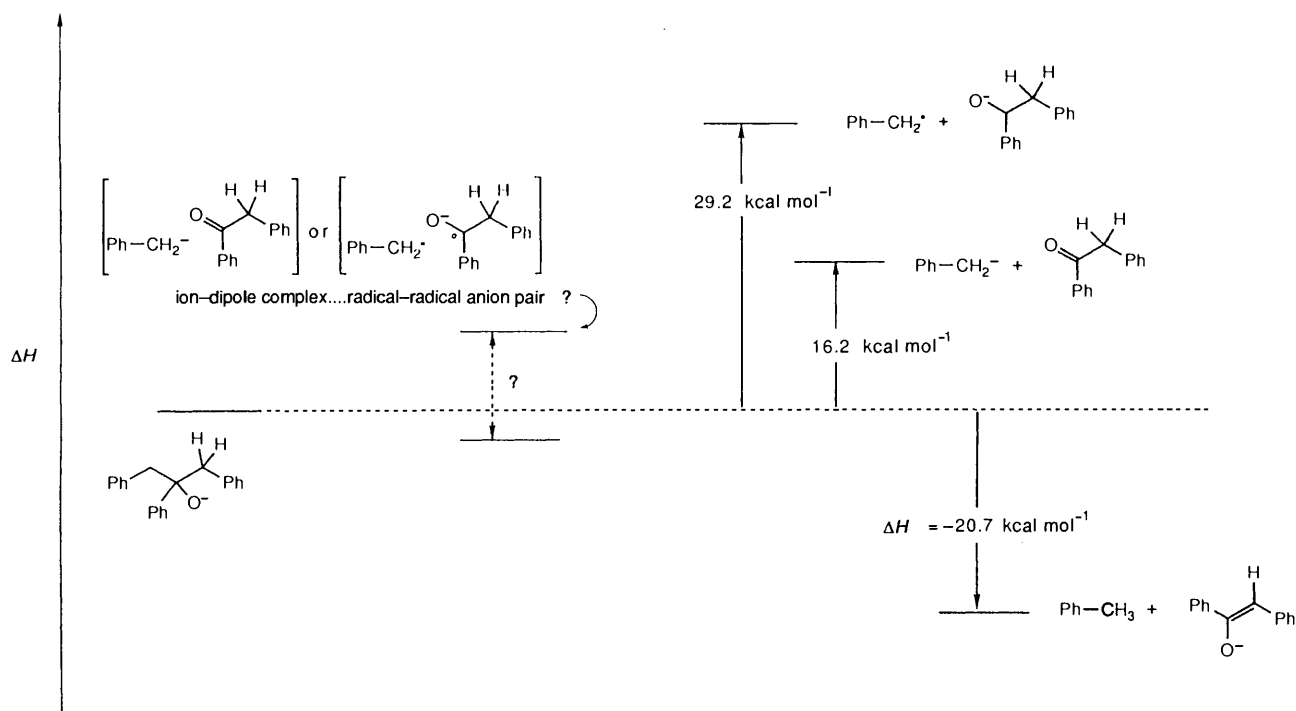


Fig. 1 Known thermochemical relationships in the gas-phase fragmentation of 1,2,3-triphenylpropoxide

observed; for CI with ammonia as the reagent only small $M + 1$ ions were observed, and measurements on the $(M + \text{NH}_4^+)$ ions gave variable results, indicating probable exchange under the CI conditions. Accurate estimates of deuterium incorporation were, however, obtained from negative ion CI mass spectra which yielded good $(M - 1)$ peaks and these measurements are detailed elsewhere in this paper.

The symmetrically dideuteriated alcohol, **1c**, was prepared by the action of α -deuteriobenzylmagnesium chloride on methyl benzoate. The alcohol is produced as a mixture of *meso* and racemic diastereoisomers with ^1H NMR spectroscopy (300 MHz) of the product mixture showing two singlets separated by 41 Hz arising from the benzylic hydrogens. Within experimental uncertainty (*ca.* $\pm 1\%$), these were of equal intensity, so that there is no evidence of isotopically-induced diastereoselection in the addition of the deuteriated Grignard reagent to deuteriated 1,2-diphenylethanone.

The unsymmetrically ^{13}C -labelled isotopomer, **1e**, was prepared using α - ^{13}C -benzyl chloride to prepare the Grignard reagent for addition to 1,2-diphenylethanone.

The Solution Experiments.—Only in the case of **1b** have kinetic isotope effects (k.i.e.) been determined by intermolecular comparison. Rates were determined by UV-spectrophotometric monitoring of formation of the enolate of deoxybenzoin in DMSO solutions of the sodium salts of **1a** and **1b** under as nearly identical conditions as possible. In each case, good first-order behaviour was observed and the combined rate data are presented in Table 1. The relatively large uncertainty in the rates, and thus the isotope effect, reflects the previously noted sensitivity of this reaction to trace amounts of moisture.⁶

Ideally, this kinetic isotope effect should be determined from rates of **1a** and **1b** reacting in the same solution. NMR spectroscopy of reacting $[^2\text{H}_6]$ -DMSO solutions of mixtures of the sodium salts of **1a** and **1b** provides a method of simultaneously monitoring their concentration changes. The ^1H NMR spectrum of a $[^2\text{H}_6]$ -DMSO solution of the sodium salt of the natural abundance alcohol, **1a**, shows a quartet

centred at δ 2.86 associated with the diastereotopic methylene protons and a complex signal at δ 7.1–7.8 from the aromatics. The spectrum evolves to yield signals which can be assigned to deuteriotoluene, which slowly exchanges benzylic hydrogens with the dimsyl solution, and to the enolate of 1,2-diphenylethanone. Notably, the enolate alkene hydrogen is well resolved as a clean singlet at δ 5.61, and when reaction mixtures are fully protected from oxygen and moisture, its integral shows no diminution over a period of weeks at room temperature. The enolate spectrum also shows a one-hydrogen triplet, centred at δ 6.89, assigned to a *para*-hydrogen on one of the phenyl groups. Since the δ 5.61 signal arises only from the product from reaction of **1a** and that at δ 6.89 from both **1a** and **1b**, their evolution with time yields the necessary rate data. The result from this experiment is also presented in Table 1. The k.i.e. thus obtained agrees with that from conventional UV-spectrophotometric methods, but again, the uncertainty is large, now reflecting reliability in integration of signals in the NMR spectra.

For all other k.i.e.s, we have relied on product analyses rather than rate measurements, and a protocol was developed to minimize possible complicating proton exchanges under the fragmentation conditions. The enolates, once produced, were not expected to exchange as long as they were in the basic dimsyl-DMSO medium of the fragmentation, and this supposition is confirmed by ^1H NMR observations presented above. Addition of dimethyl sulfate at the end of the reaction efficiently traps the enolates as their methyl ethers, with practically no *C*-alkylation for either potassium or sodium salts.¹⁴ GC-MS comparison with authentic samples showed that the *Z*- and *E*-isomers were formed in greater than 20:1 ratio. These gave strong molecular ions in their positive EI mass spectra which were used for determination of deuterium incorporation.

In some cases, isotopic incorporations in the toluene was also determined. Under these conditions, slow exchange of benzylic protons in the toluenes may be expected, and indeed is observed in reactions monitored by ^1H NMR spectroscopy. For product analysis, reactions were therefore run in an apparatus which

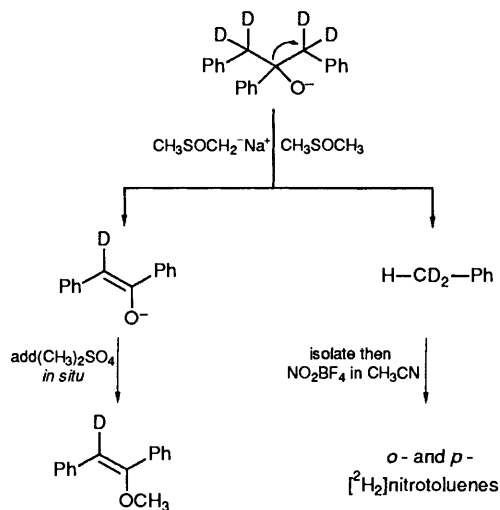
Table 1 Rate data and kinetic isotope measurements in fragmentations of **1a** and **1b** in DMSO solution

Reactant	Label	Method	T/°C	[NaDimethyl]/mol dm ⁻³	[ROH]/mol dm ⁻³	k _{obs} /10 ⁻⁴ s ⁻¹	k _{H₄} /k _{D₄}
1a	[² H ₀]	UV	30.4	0.035	5 × 10 ⁻⁵	10.46 (±0.95) ^a	
1b	[² H ₄]	UV	30.4	0.035	5 × 10 ⁻⁵	6.08 (±0.25) ^a	1.72 (±0.23)
1a	[² H ₀]	NMR	21	0.094	0.048	1.39 (±0.07) ^b	
1b	[² H ₄]	NMR	21	0.094	0.048	0.85 (±0.10) ^b	1.63 (±0.27)

^a Mean and SD of three measurements. ^b Uncertainties are SDs of the fit from the non-linear regression analysis.

allowed the volatile products to be pumped from the basic solutions as they were formed and collected in a cold trap. Mass spectrometric determination of deuterium in toluene is complicated by the loss of hydrogen under EI ionization¹⁵ to yield benzyl or tropylium ions. It has been suggested that low ionization energies can reduce this problem¹⁶ but, in our hands, ionization at 15 eV gave ion currents too low for reliable measurements. We therefore treated the isolated toluenes with nitronium tetrafluoroborate and determined deuterium content in the resulting nitrotoluenes. Suhr and Zollinger¹⁷ report that there is no secondary k.i.e. in the nitration of α -[²H₃]-toluene so that incorporations should accurately reflect those in the toluene precursors. The *para*-isomers yield excellent molecular ions and intensity ratios were highly reproducible: these were less so for the *ortho*-isomers, possible because of a competing loss of hydroxide and water¹⁸ involving hydrogens at the methyl group.

Experiments with sodium or potassium salts of the tetra-deuterated alcohol, **1b**, provided a control on the analytical protocol (Scheme 3). The reaction yielded monodeuterated enol ethers. Deuterium incorporations were high, but perhaps a little lower in the sodium salt product than in that from the potassium salt, probably showing some exchange occurring in the longer reaction times required for reaction of the sodium salts. Similarly, α,α -[²H₂]-nitrotoluenes were isolated with isotopic incorporation corresponding to that in the alcohol itself, confirming, incidentally, that the additional hydrogen appearing in the toluene is derived from solvent rather than from the ketone.



Scheme 3 Fragmentation of 1,1,3,3-tetradeuterio-1,2,3-triphenylpropoxide in DMSO

For the product analyses from the doubly deuterated alcohols, **1c** and **1d**, both sodium and potassium salts were again used, and the combined data for both sodium and potassium salts is presented in Table 2. We believe that the uncertainties in the product deuterium incorporation ratios are $\pm 10\%$ of their values, and that there is no significant difference between the

results from sodium and potassium salts, although the data suggest that the enol ether products from sodium salts give a slightly lower incorporation ratio, again probably because the longer reaction times increase the chance of undesired exchanges.

The intramolecular effect of isotopic substitution at the reacting carbon-carbon bond in **1e** has been examined both by ¹H NMR monitoring of the reaction and by the more conventional product analytical methods detailed above for the hydrogen isotopomers. When the decomposition of the sodium salt of **1e** in [²H₆]-DMSO is monitored by ¹H NMR spectroscopy the signal from the alkene hydrogen of the product enolate shows the expected ¹³C-satellites with $J_{(C-H)} = 147.2$ Hz (see Fig. 2). Careful integration over the signal yielded the isotope distribution in the enolate, and the resulting fractionation ratio, after correction for incomplete labelling in the alcohol, is ¹³C: ¹²C = 1.045 (±0.007). The expected satellites in the methyl signal from the toluene are also observable, but accurate integration is not possible because of signals from residual protic DMSO in the solvent.

Unquantifiable systematic errors associated with phasing of the spectra lead us to view the ratio thus obtained with some reservations. The labelling ratio in the enolate product was also determined separately by the conventional analytical methods outlined above. The sodium salt of **1e** was allowed to react in all-H DMSO, and the enolate alkylated as before for mass spectral analysis. The incorporation thus found (see Table 2) is in the same sense, and slightly larger than by the NMR integration. Although the values overlap within their experimental uncertainties, we believe that the mass spectroscopic result is the more reliable.

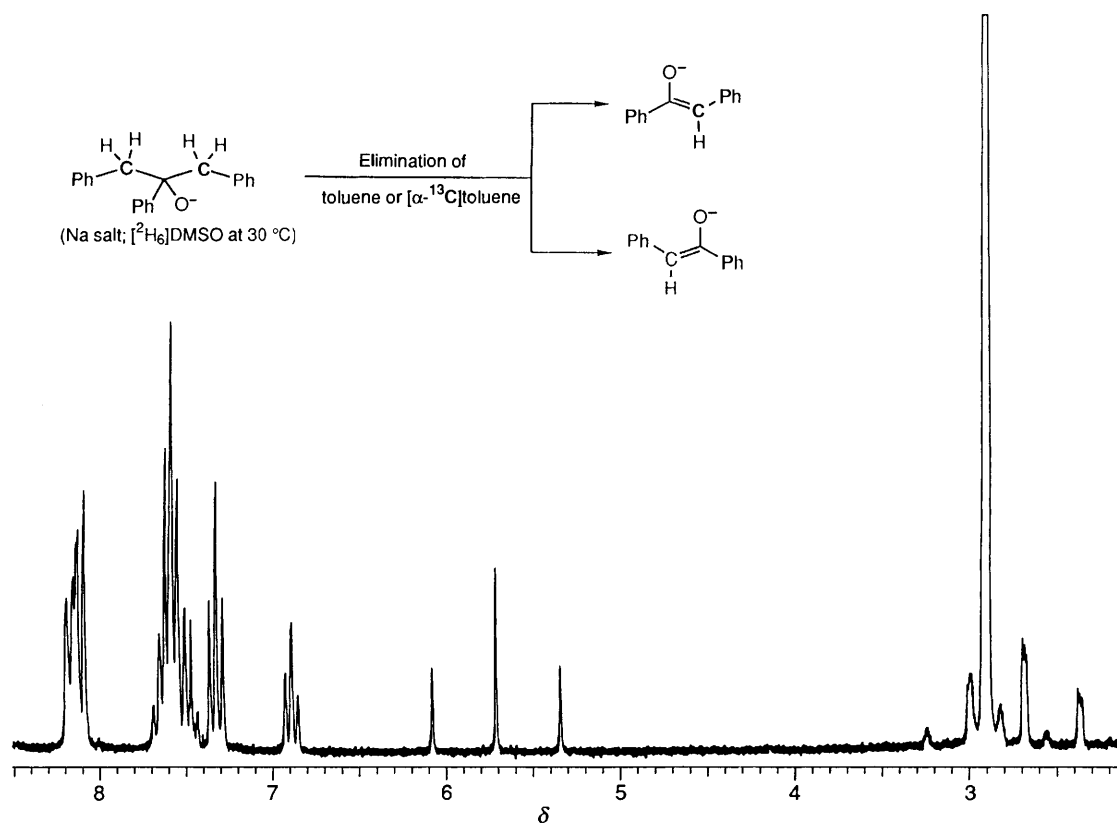
The Gas Phase Experiments.—The negative chemical ionization spectrum of **1a** is extremely simple. When the alcohol reacts with BuO⁻ in the source of a mass spectrometer¹⁹ only three alcohol-derived ions are observed. Those at $m/z = 287$ (24%) and $m/z = 195$ (100%) were shown by accurate mass measurement, and analysis of peak intensities (assuming natural abundance isotopic distributions) to have molecular formulae C₂₁H₁₉O and C₁₄H₁₁O, respectively, corresponding to deprotonated alcohol and 1,2-diphenylethanone enolate. Linked scanning established a parent-daughter relationship between these ions. The third peak, $m/z = 269$, did not appear reproducibly, its intensity depending strongly on heating rates and cleanliness of the probe. We believe it to be 1,2,3-triphenylpropenide, C₂₁H₁₇⁻, formed by deprotonation of 1,2,3-triphenylpropene, in turn formed by dehydration of the alcohol on the probe. This peak was completely absent when probe temperatures and heating rates were as specified in the Experimental section and was not investigated further.

With **1b**, the peaks appear at $m/z = 291$ and 192, corresponding to [²H₄]-alkoxide and [²H₁]-enolate. These intensity ratios in each group of peaks were highly reproducible and label incorporations determined mass spectrometrically in the alkoxide and by ¹H NMR integration of the alcohol showed that there was no measurable loss of label in the alkoxide. The label incorporations in **1c**, **1d** and **1e** were all reliably de-

Table 2 Isotopic incorporations in alcohols **1a** to **1e** and in products of reaction of their sodium and potassium salts in DMSO at 30 °C

Reactant	Label	Reactant alcohol	Reaction products (K salts)		Reaction products (Na salts)	
			Enol ether ($[^2\text{H}_1]/[^2\text{H}_0]$)	Toluene ($[^2\text{H}_0]/[^2\text{H}_2]$)	Enol ether ($[^2\text{H}_1]/[^2\text{H}_0]$)	Toluene ($[^2\text{H}_0]/[^2\text{H}_2]$)
1a	$[^2\text{H}_0]$	100.0	100.0	100.0	100.0	100.0
1b	$[^2\text{H}_4]$	91.8				
	$[^2\text{H}_3]$	8.2				
	$[^2\text{H}_2]$			95.1		96.0
	$[^2\text{H}_1]$		92.0	4.4	88.3	3.8
	$[^2\text{H}_0]$		8.3	0.4	12.3	
1c	$[^2\text{H}_2]$	95.1				
	$[^2\text{H}_1]$	3.9	71.5 (2.77) ^a	98.1	70.7 (2.56) ^a	97.6
	$[^2\text{H}_0]$	1.4	28.5	1.9	30.2	2.3
1d	$[^2\text{H}_2]$	92.2		37.5		37.0
	$[^2\text{H}_1]$	6.4	56.3 (1.40) ^a	2.0 (1.47) ^a	55.3 (1.34) ^a	3.1 (1.44) ^a
	$[^2\text{H}_0]$	1.4	43.7	60.4	44.7	58.7
1e	$^{13}\text{C}_1$	99.4			51.23 $^{13}\text{C}/^{12}\text{C}$	
	$^{13}\text{C}_0$	0.6			48.77 (1.064 ± 0.009) ^b	

^a Calculated assuming that $[^2\text{H}_0]$ -alkoxide yields only $[^2\text{H}_0]$ -product and $[^2\text{H}_1]$ -alkoxide yields equal amounts of $[^2\text{H}_1]$ - and $[^2\text{H}_0]$ -product. Taking each of the incorporations to be ±0.5%, the error in each ratio is *ca.* ±8% of its value. ^b Mean and SD repeated spectra of the reaction product. Ratio is corrected for incomplete labelling.

**Fig. 2** Fragmentation of $[1\text{-}^{13}\text{C}]$ -1,2,3-triphenylpropoxide

terminated by analysis of peak intensities of the molecular ion ($M - 1$) peaks.

There are clearly parallels between the gas and solution phase reactions of the alkoxide, with clean elimination of toluene occurring in both cases. Mass spectrometry affords a relatively simple method of examining the reaction in the absence of solvent, and the NCI mass spectra of all the isotopomeric alcohols were examined under standard conditions. Label incorporations in the fragmentation product are presented in Table 3.

Additionally, measurements were made of relative abundances of the daughter ions from the alkoxide parents using *B/E* linked scans. The alkoxide decompositions thus observed

are unimolecular metastable processes in which the parent ion energy is minimal.²⁰ Control experiments with **1a** and **1b** established that it was possible to select daughters of a single isotopomer with less than 0.1% contribution from daughters of parents separated by a single mass unit. The data is also presented in Table 3.

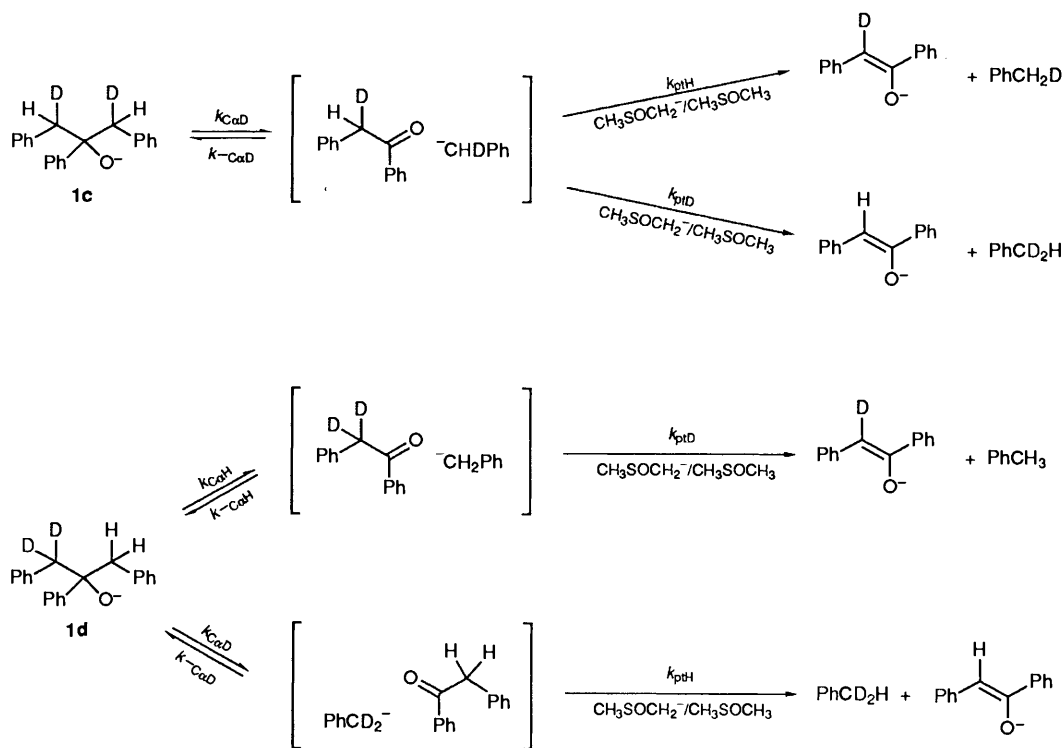
Discussion

We examine first the data from the solution experiments, and, in the absence of evidence to the contrary, we describe the reaction sequence as ionic rather than radical processes. As noted above, the products from **1b** confirm the involvement of solvent as

Table 3 Isotopic incorporations in alcohols **1a** to **1e** and in enolates in mass spectrometric fragmentations

Reactant	Label	Reactant alcohol	Enolate compositions		Product ratios	
			Conventional scan	Linked scan	Conventional scan	Linked scan
1a	[² H ₀]	100.0	100.0	100.0		
1b	[² H ₄]	91.8				
	[² H ₃]	8.2				
	[² H ₂]		99.0	99.0		
	[² H ₁]					
1c	[² H ₂]	95.1				
	[² H ₁]	3.9	66.0	71.2	2.09 ^a	2.47 ^b
	[² H ₀]	1.4	34.0	28.8		
1d	[² H ₂]	92.2				
	[² H ₁]	6.4	41.0	41.8	0.77 ^a	0.72 ^b
	[² H ₀]	1.4	56.6	58.2		
1e^d	¹³ C ₁	99.4	51.65	52.00		
	¹³ C ₀	0.6	48.35	48.00	1.082 ^c	1.083 ^b

^a Ratios calculated assuming that [²H₀]-alkoxide yields only [²H₀]-enolate and [²H₁]-alkoxide yields equal amounts of [²H₁]- and [²H₀]-product. Taking ±0.5% error in the incorporations gives an error in the ratio of about ±8% of its value. ^b Ratios from averaged spectra. Standard deviation ±3% of the tabulated value. ^c Ratio is corrected for incomplete labelling and is the average of results from a number of spectra. Standard deviation is ±0.033. ^d The label here is excess over natural abundance.

**Scheme 4** Solution fragmentations of **1c** and **1d**

proton source and dimsyl anion as base in the formation of enolate and toluene from the intermediate ketone and benzyl anion. In the reactions of **1c**, **1d** and **1e**, the product ratios measure energy differences of pairs of isotopomeric transition states relative to each of the reactant ground states. Since each pair of products arises from a common ground state, there can be no contribution of ground state energies difference to the product distribution from that reactant.

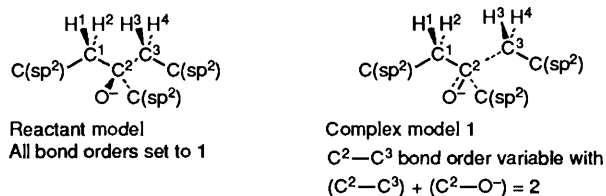
Scheme 4 shows the reaction scheme for products from **1c**. The labelling is symmetrically disposed in the benzylic groups, so that cleavage of either of the benzylic C–C bonds yields the same intermediate. The ratio of enol ether products (average

from sodium and potassium [²H₁]/[²H₀] = 2.67) therefore measures the primary kinetic hydrogen isotope effect, k_H/k_D , on the proton transfer event, modified by a (probably) small secondary α -deuterium effect on the proton transfer,²¹ irrespective of which step is rate determining. The effect is well below the theoretical maximum for proton transfers between carbons, but is consistent with the unsymmetrical transition structure expected in the exothermic transfer (21.4 kcal mol⁻¹)²² from 1,2-diphenylethanone to dimsyl anion. In protonation of benzyllithium or benzylmagnesium chloride by water or other oxygen acids the effects are <1.5.²³

With the unsymmetrically deuteriated **1d**, the simplest

Table 4 Calculated primary carbon and secondary α -hydrogen kinetic isotope effects using complex 1 for compounds **1b**, **1d** and **1e**

Complex bond order C(2)–C(3)	Complex $\nu(\text{imag})/\text{cm}^{-1}$	Isotope labelling patterns and rate ratios		
		1 All H and ^{12}C 2 H_1 to $\text{H}_4 = \text{D}$ k_1/k_2 (1b)	H_1 and $\text{H}_2 = \text{D}$ H_3 and $\text{H}_4 = \text{D}$ k_1/k_2 (1d)	All H and ^{12}C C(3) = ^{13}C k_1/k_2 (1e)
0.9	59.6	1.063	1.059	1.018
0.7	108.9	1.164	1.160	1.030
0.5	148.8	1.294	1.293	1.043
0.4	168.1	1.376	1.376	1.049
0.3	187.6	1.476	1.477	1.056
0.2	208.0	1.603	1.605	1.063
0.1	230.1	1.784	1.786	1.070

**Fig. 3** Reactant and complex models used in the BEBOVIB calculations

interpretation, shown also in Scheme 4, arises when proton transfer is fast compared to events preceding it, *i.e.*, $k_{\text{pt}} > k_{\text{c}}$. These may be carbon-carbon bond cleavage, or perhaps insertion of solvent into a resulting ion-dipole complex, but we make no distinction at this stage. In that case the $[\text{H}_1]/[\text{H}_0]$ ratio in the enol ether product or the $[\text{H}_0]/[\text{H}_2]$ ratio in the toluenes measures the secondary α -deuterium k.i.e. The ratios, 1.37 and 1.46, respectively (~ 1.2 per D), are in the expected sense for a tetrahedron to trigonal reorganization at the benzylic carbon,²⁴ but are large in comparison to those commonly observed in formal substitutions at benzylic carbon whether by concerted processes or by mechanisms thought to involve radical or carbocationic intermediates.²⁵ Within the same framework, the observed $^{13}\text{C}/^{12}\text{C}$ ratio in the enol ether products from fragmentation of **1e** has to be identified with a primary ^{13}C kinetic isotope effect, $k_{^{12}\text{C}}/k_{^{13}\text{C}} = 1.065 \pm 0.007$, on the cleavage yielding benzylic anion. Again, the ratio is large compared with most carbon effects for formal substitutions at benzylic carbons.²⁶ The results, from both **1d** and **1e** can only be consistent with the rate limiting C–C cleavage if there is a relatively high degree of bond breaking in the transition state without compensating bond-making at the isotopically-substituted sites.

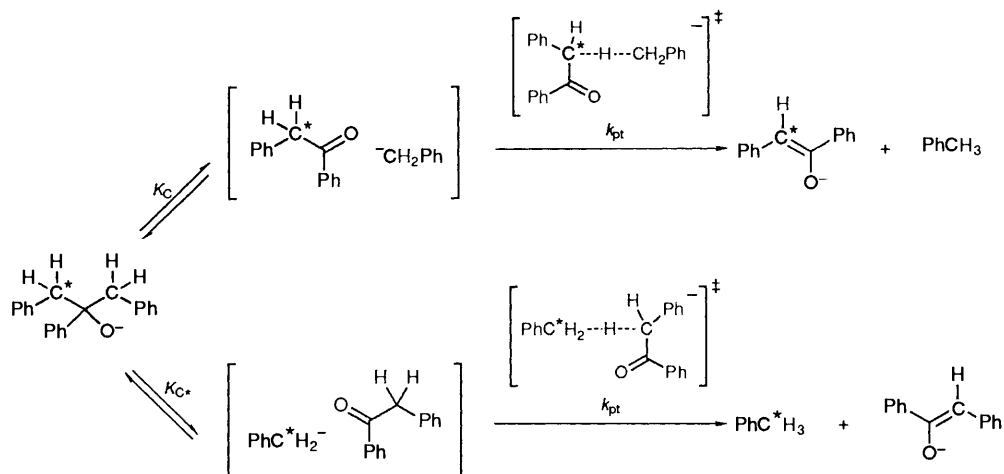
Calculations using the bond energy-bond order treatment of Sims²⁷ on simple transition structure models support this interpretation. The models adopted for the reactant and the complex are shown in Fig. 3. For complex 1, an imaginary frequency was generated by coupling of the C(2)–C(3) and C(2)–O[−] bond stretching vibrations with a coupling constant of 1.1. No further interaction constants were used. For a series of labelling patterns, the C(2)–C(3) bond order in the complex was then varied while maintaining valence at C(2) to model transformation of the alkoxide to the carbanion-ketone complex. The results, using the standard set of force constants for vibrations with the BEBOVIB-IV program²⁸ are presented in Table 4. Column **1d** models the experiments yielding the product labelling ratios from reaction of **1d**. As expected the rate ratios increase with decreasing C(2)–C(3) bond order in the activated complex and the experimental values are best matched by low bond orders of 0.3 to 0.2. The calculated effects for the labelling pattern corresponding to the experiment with **1e** are shown in column **1e** of Table 4. The match with this experiment is best for a C(2)–C(3) order of

0.2, so there is a pleasing consistency between the light and heavy atom results.

Taking the average of the two methods used, the rate measurements on **1a** and **1b** yield an intermolecular k.i.e., $k_{\text{H}_4}/k_{\text{D}_4} = 1.68$, which is notably larger than the intramolecular effect in **1d** although both experiments should measure the secondary α -deuterium effect on the C–C bond cleavage step. The additional labelling alone in **1b** is not expected to contribute greatly to the isotope effect provided that the reactant ground states are the same, and this is confirmed by calculations, the results of which are shown in column **1b** of Table 4, using the same model of reactant and complex with appropriate labelling patterns. However, intramolecular and intermolecular comparisons differ in that rate ratios from intermolecular measurement contain a contribution to activation energy differences from reactant ground states. In these DMSO solutions, the sodium alkoxides exist as ion-pairs ($K_{\text{ip}} \sim 10^4$) and the pseudo-first-order rate constants determined pertain to disappearance of total alkoxide. We suggest that there are additional steric compressions in the ion-paired alkoxides which have the effect of raising force constants at the isotopically-substituted sites and thereby emphasize the difference between the salts of **1a** and **1b** in solution. It follows that there should be a difference in the ion-pairing constants of **1a** and **1b**. We have no experimental confirmation on this point, but steric compression in ground states has previously been postulated as a cause of large α -deuterium k.i.e.s in substitutions at benzylic carbon, although not by carbanionic mechanisms.²⁹

Measurements of α -deuterium k.i.e.s associated with the formation of carbanions are rare, and none are known for the specific case of benzyl. For related examples, Murdoch³⁰ reports an equilibrium α -deuterium isotope effect on formation of the fluorenyl anion (Li salt in THF), $K_{\text{H}}/K_{\text{D}} = 1.19$. More recently and more relevantly, Gajewski and Gee³¹ have measured the α -deuterium k.i.e. for the anionic oxycope rearrangement of 4,4-dideuterio-3-methylhexa-1,5-dien-3-ol to the enolate of 7,7-dideuteriohept-6-en-2-one. For potassium salts in DMSO, they find $k_{\text{H}_2}/k_{\text{D}_2} = 1.67 (\pm 0.05)$, the largest ever reported α -deuterium effect, taken to indicate a highly dissociative mechanism for the rearrangement, with near complete cleavage of the bond from allyl to the alkoxide carbon yielding a complex of allyl anion and methyl vinyl ketone. This large k.i.e. was also the result of intermolecular comparison, and thus also includes a possible effect from alkoxide ion pairing. We suggest that our measurements are consistent with analogous rate-limiting formation of a benzyl anion–1,2-diphenylethanone complex, again with a high degree of bond cleavage in the transition structure.

In the mass spectrometry, the isotopic incorporations in the daughter enolates show that there are also isotope effects on the gas phase fragmentations. From available thermochemical data, deprotonation of **1** by BuO^- should be exothermic⁸ by no more than 4 kcal mol^{−1} so that the decomposing ions are



Scheme 5 Gas-phase fragmentation of [1-¹³C]-1,2,3-triphenylpropoxide

unlikely to be excited either electronically or vibrationally. For kinetic energies within the ensemble of reacting ions, it is unlikely that Boltzmann distributions are obtained,³² although pressures in CI sources are relatively high, so that some thermal equilibration occurs. Generally, the data in Table 2 show that selectivities are larger in the linked scans than in the conventional spectra, although the differences are not large. Presumably, this reflects the kinetic energy selection inherent in the *B/E* linked scan experiment.

In discussing the gas phase experiments, we again adopt the polar description, viewing the reaction as proceeding through a short-lived complex of benzyl anion and 1,2-diphenylethanone. Under the mass spectrometric conditions, intermolecular processes can not occur after the initial formation of the parent ion, and the formation of enolate from the ion-dipole complex must involve an intra-complex proton transfer from the ketone to the benzyl anion. As with the solution experiments, the isotope ratio, $[^2\text{H}_1]/[^2\text{H}_0] = 2.47$, in the enolates from **1c** measures the primary deuterium, k.i.e. on the hydron transfer step irrespective of which step is rate limiting. The value is slightly smaller than that found in solution where the transfer is from the ketone to dimsyl, perhaps to be expected in view of the more exothermic transfer (36 kcal mol^{-1}) to benzyl anion. The value also fits the pattern of k.i.e.s reported for gas-phase transfers of proton from acetone to a series of carbon bases including CF_3^- , Ph^- and CH_3^- , where the exothermicities are 7, 28 and 48 kcal mol^{-1} , respectively.³³ For Ph^- and CH_3^- , the primary k.i.e.s are 2.5 and 1.6, bracketing our measurement, despite the fact that these are anions with localized negative charge.

The behaviour of **1d** demonstrates a difference between the gas and solution reactions. If events prior to proton transfer are also rate limiting in the gas phase reaction, the effect, $[^2\text{H}_1]/[^2\text{H}_0] = 0.75$ would have to be identified with a secondary α -deuterium effect on formation of benzyl anion. We reject this hypothesis since we know of no example of an inverse α -deuterium k.i.e. on a tetrahedral to trigonal reorganization at carbon, and can find no sensible combination of force constants which would yield this value in computational studies with complex **1** which models the bond-breaking TS. If, however, the proton transfer step to benzyl is rate limiting, then the observed ratio can be identified with the α -deuterium effect on the equilibrium between the isotopomeric ion-dipole complexes, divided by the primary deuterium effect on the hydron transfer. Combining the data from **1c** and **1d** allows an estimate of the α -deuterium E.I.E., $K_{(\text{d},2)} = 0.72 \times 2.47 = 1.78$, which is not incompatible with the results of the computational studies in Table 3 although BEBOVIB-IV calculations may not be

entirely appropriate for the study of non-equilibrated ions.³⁴ Within the same framework, the product ratio in the fragmentation of **1e**, see Scheme 5, should reflect a ¹³C-equilibrium isotope effect on the fragmentation, K_C/K_{C^*} , expected to be a little greater than 1.07, modified by the ratio of the primary ¹³C-isotope effects on the strongly exothermic proton transfers in the complexes. The latter should be very close to unity; carbon isotope effects on proton transfers are small,³⁵ and in this ratio, both rates are affected with transfer from a ¹³C site in one case to a ¹³C site in the other.

To conclude, we speculate briefly on the origins of the differences between solution and gas phase reactions. We first consider the nature of the gas phase reaction, then the effect of 'solvating' each intermediate or transition structure with a single molecule of DMSO.³⁶ Proton transfers between charge delocalized ions (the case here) in the gas phase can be inefficient even when energetically favourable,³⁷ for example, Han and Brauman have been able to model the rate-equilibrium behaviour of gas-phase proton transfers between substituted benzyl anions using the Marcus³⁸ relationship, eqn. (4), with an intrinsic barrier, $\Delta E_0^* = 7 \text{ kcal mol}^{-1}$.

$$\Delta E^* = (\Delta E^\circ)^2 / (16\Delta E_0^*) + \Delta E_0^* + 1/2\Delta E^\circ \quad (4)$$

With this intrinsic barrier, the form of the relationship means that the Marcus barrier (ΔE^*) to a transfer occurring in the ion-dipole complex would vanish if the reaction were exothermic (ΔE°) by more than 28 kcal mol^{-1} . As shown in Fig. 1, the conversion of benzyl anion and deoxybenzoin into toluene and deoxybenzoin enolate is exothermic by 36 kcal mol^{-1} . The existence of a barrier to proton transfer thus depends on the relative magnitude of the ion-dipole stabilizations in each of the complexes. If we assume 15 kcal mol^{-1} for ion-dipole stabilization of the benzyl anion-ketone complex and none for the hydrocarbon-enolate complex then the complex to complex exothermicity will be *ca.* 21 kcal mol^{-1} ; the Marcus relationship then yields a barrier for the proton transfer³⁹ interconverting the two complexes of only $0.5 \text{ kcal mol}^{-1}$. The value of $\Delta E_0^* = 7 \text{ kcal mol}^{-1}$ is probably too low since the intrinsic barrier for proton transfer between the enolates would be expected to be higher than for benzyl anions. However, even with $\Delta E_0^* = 10 \text{ kcal mol}^{-1}$, $\Delta E^* = 2.2 \text{ kcal mol}^{-1}$. The unavoidable implication is that the barrier to C-C bond cleavage is very low indeed, perhaps with the alkoxide being only a transition structure between the two ion-dipole complexes formed by extension of either the C(1)-C(2) or C(2)-C(3) bonds of the alkoxide. A potential energy profile for the gas phase reaction might then be as shown in Fig. 4.

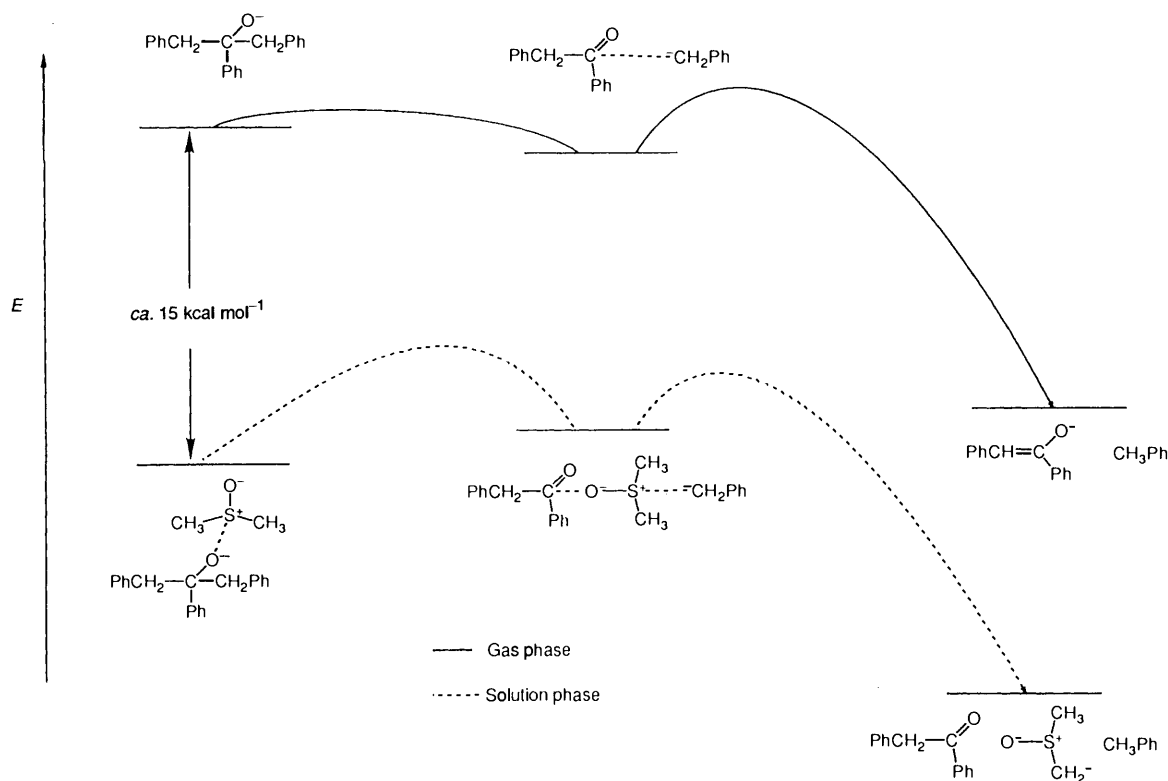


Fig. 4 Energy profiles for gas and solution fragmentations

In presence of a molecule of DMSO, there will be a stabilizing interaction between the localized charge of the alkoxide and the sulfoxide dipole. Studies on gas-phase clustering of halides with DMSO give $\Delta H = -18.6$, -17.3 and -15.7 kcal mol⁻¹ for chloride, bromide and iodide, respectively, in formation of the 1:1 X⁻:Me₂SO complex. For the sake of argument, we take 15 kcal mol⁻¹ as a working estimate for the stabilizing interaction of the alkoxide and a DMSO molecule. The effect of adding a DMSO molecule to the benzyl anion–ketone complex with its delocalized charge should be less, particularly since the DMSO molecule can be regarded as displacing a polar ketone in interacting with the anion. The initial intermediate might now be viewed as the result of insertion of the DMSO molecule into the benzyl anion–ketone complex, and the barrier to this more complex molecular reorganization would be larger than the simple bond extension of the gas phase reaction. Since the charge on CH₃SOCH₂⁻ is localized,⁴⁰ proton transfers involving DMSO are expected to be kinetically favoured over those involving carbon acids of comparable acidity which yield delocalized anions.⁴¹ The barrier to proton transfer leading to products in the 'solvated' complex might be comparable with that in the gas phase ion–dipole complex, despite its lower exothermicity. Fig. 4 also shows a speculative energy profile for the 'solution' reaction.

Experimental

GLC was carried out on a Carlo Erba 4130 chromatograph fitted with a capillary column (5 m × 0.22 mm) with an 0.25 μm OV-1 cross-bonded stationary phase, and hydrogen at 1 cm³ min⁻¹ as carrier gas. Merck pre-coated silica plates (0.25 mm Kieselgel 60 F₂₅₄) were used for analytical TLC and 20 × 20 cm plates coated with Merck Kieselgel 60 PF₂₅₄ at 20 g per plate for preparative TLC. Kieselgel H and a range of solvents, all distilled before use, were used in column chromatography. IR spectra were recorded on a Perkin-Elmer 1710-FT spectrometer, routinely on thin films on NaCl plates. UV spectra

were recorded on a Shimadzu UV-260 spectrometer on solutions in 95% aqueous ethanol. Routine ¹H and ¹³C NMR spectra were run on a Bruker AC 300E spectrometer operating at 300 and 75 MHz, respectively. Chemical shifts are reported in ppm (δ) relative to internal TMS and coupling constant values *J* in Hz. Melting points were determined on a Kofler hot stage microscope and are uncorrected. Microanalyses were run at the University of Manchester Microanalytical Laboratory under the direction of Mr. M. Hart. Water contents were determined by coulometric Karl–Fisher titration. Ether refers to diethyl ether throughout. Light petroleum refers to the fraction boiling at 40–60 °C.

Dimethyl sulfoxide (DMSO) and dimsyl solutions. DMSO was purified by distillation under reduced pressure from sodium amide following the method of Bordwell *et al.*⁴² Sodium or potassium dimsyl were prepared by reaction of the alkali metal amide under argon atmosphere at room temperature as described in earlier work. Concentrations of base were determined by titration of diphenylacetic acid⁴³ using inert gas line transfers and gas tight syringes.

1,2,3-Triphenylpropan-2-ol (1a).—(General procedure for addition of benzylmagnesium chloride to 1,2-diphenylethanones). Magnesium turnings (0.24 g, 10.0 mmol) were placed in an RB flask fitted for reflux, stirring and inert atmosphere. The assembly was flamed under nitrogen flow then cooled before slow addition of a solution of benzyl chloride in ether (1.27 g, 10 mmol, in 10 cm³). When all the magnesium was consumed (*ca.* 1 h) a solution of 1,2-diphenylethanone in ether (1.46 g, 7.5 mmol in 10 cm³) was added slowly to the stirred Grignard reagent. After complete addition, the mixture was refluxed for 30 min before being cooled, and poured into cold, stirred aqueous HCl (50 cm³; 1 mol dm⁻³). Separation and ether extraction yielded a combined ether layer (50 cm³) which was dried (MgSO₄), and evaporated to yield a solid. Recrystallization from aqueous ethanol yielded white crystals (1.89 g, 88%) m.p., 85.0–86.5 °C (lit.,⁴⁴

85–86 °C); δ_c 48.59 (t), 76.67 (s), 125.56 (d), 126.26 (d), 127.56 (d), 127.65 (d), 130.49 (d), 136.14 (s) and 145.03 (s) (Found: C, 87.1; H, 7.0. $C_{21}H_{20}O$ requires C, 87.46; H, 6.99%).

2,2-Dideuterio-1,2-diphenylethanone. 1,2-Diphenylethanone (3.9 g, 19.9 mmol) and dry distilled dioxane (10 cm³) were placed in an RB flask fitted for stirring, reflux and inert atmosphere. Potassium carbonate (0.21 g) and D₂O (10 cm³) were added and the mixture was stirred at 85–90 °C for 48 h. ¹H NMR spectroscopy then indicated near complete loss of the methylene signal at δ 4.2. The cooled mixture was extracted with ether and the dried (MgSO₄) extracts evaporated to yield a light yellow solid (3.61 g), which was again subjected to exchange with a fresh portion of D₂O. Work-up as before, and bulb-to-bulb distillation (120–125 °C at 0.5 mmHg) and recrystallization from light petroleum yielded crystals (2.35 g), m.p. 53.5–54.5 °C (lit.,* 55.0–56.6 °C). Mass spectrometry (+ve Cl) gave deuterium content [²H₁] 5.9 to [²H₂] 88.5%. ¹H NMR spectroscopy gave [²H₂] 95%.

1,1,3,3-Tetradeterio-1,2,3-triphenylpropan-2-ol (1b). 1,3-Diphenylpropanone was treated with potassium carbonate and D₂O in dioxane as described above for the deuteration of 1,2-diphenylethanone. The crude product showed high deuterium content (>90% [²H₄] by ¹H NMR spectroscopy) and was used directly in preparation of the alcohol. Phenylmagnesium chloride (10 mmol) and the tetradeteriated ketone (1.2 g) following the procedure of Partington *et al.*⁶ yielded the alcohol as crystals (0.98 g, 62%) after crystallization from light petroleum, m.p. 86–87 °C (lit.,⁴⁴ 85–86 °C) (Found: C, 86.8; H, 6.8. $C_{21}H_{20}O$ requires C, 87.46; H, 6.99%). Mass spectrometric analysis (–ve Cl) gave deuterium incorporation shown in Table 2.

1,1-Dideuterio-1,2,3-triphenylpropan-2-ol (1d). Addition of benzylmagnesium chloride to 2,2-dideuterio-1,2-diphenylethanone (1.98 g) using the general method described above yielded crystals (1.28 g, 44%), m.p. 85.5–86 °C (lit.,⁴⁴ 85–86 °C) (Found: C, 87.4; H, 6.95. $C_{21}H_{20}O$ requires C, 87.46; H, 6.99%). Mass spectrometric (–ve Cl) analysis gave deuterium incorporation shown in Table 2.

1,3-Dideuterio-1,2,3-triphenylpropan-2-ol (1c). An ethereal solution of α,α -dideuteriobenzylmagnesium chloride was prepared from α,α -dideuteriobenzyl chloride⁴⁶ (2.5 g, 20 mmol) and magnesium by the method described above. A solution of methyl benzoate in ether (1.4 g, 10 mmol in 50 cm³) was added dropwise over 30 min to the cooled solution which was then refluxed for a further 30 min. Standard work-up with aqueous HCl and ether extraction yielded a viscous oil which TLC showed to be a complex mixture containing a single major component. Chromatography on alumina, eluting with an ether–hexane gradient, and recrystallization from ether–hexane yielded crystals (1.84 g, 63%), m.p. 86.0–87.0 °C (lit.,⁴⁴ 85–86 °C) (Found: C, 87.5; H, 7.1. $C_{21}H_{20}O$ requires C, 87.46; H, 6.99%). Mass spectrometric analysis (–ve Cl) gave deuterium incorporation shown in Table 2.

[1-¹³C]-1,2,3-Triphenylpropan-2-ol (1c). α -¹³C-Benzyl chloride (Aldrich 99.4% ¹³C) was converted into its Grignard reagent and then allowed to react with 1,2-diphenylethanone as described above. Standard work-up and isolation yielded crystals, m.p. 86.0–87.0 °C (lit.,⁴⁴ 85–86 °C) (Found: C, 87.2; H, 7.3. $C_{21}H_{20}O$ requires C, 87.46; H, 6.99%). Mass spectrometric analysis (–ve Cl) gave ¹³C₁ 99.4%; ¹H NMR spectrum was similar to the unlabelled material but the benzylic hydrogens showed 1- and 2-bond ¹³C–H couplings of 127.0 and 2.4 Hz, respectively.

(E) and (Z)-1,2-Diphenyl-1-methoxyethene. Authentic samples were prepared by the method of Tsujihara *et al.*⁴⁷

Isolation and Product Analysis for Solution Fragmentations.—For any particular experiment, the procedures were carried out in parallel on samples of deuteriated and undeuteriated 1,2,3-triphenylpropan-2-ols. The resulting nitrotoluenes and 1,2-diphenyl-1-methoxyethenes were then compared mass spectrometrically. The reaction vessel was a jacketed flask fitted with stirring and syringe inlet which was mounted on a vacuum line with inert gas manifold. The reaction vessel could be evacuated to the gas line through a liquid nitrogen cooled trap. The alcohol (*ca.* 0.27 g) was weighed into the vessel which was mounted on the line and placed under an argon atmosphere. Water at 30 °C was circulated through the jacket, and dry DMSO (34 cm³) was then added by syringe and stirred to dissolve the alcohol. The reaction vessel was then isolated from the trap and sodium or potassium dimethyl solution (16 cm³ of *ca.* 0.06 mol dm^{–3} solution) added quickly by syringe. The valve to the trap was then opened cautiously to avoid frothing, and the reaction allowed to run for 15 min (potassium salts) or 60 min (sodium salts). The vacuum was then released to argon and dimethyl sulfate (2.0 cm³) added by syringe to the reaction vessel. After 30 min, the contents of the vessel were poured into cold aqueous NaOH (50 cm³; 0.5 mol dm^{–3}) and shaken. The organic products were extracted with CCl₄ (5 cm³), dried and stored over anhydrous K₂CO₃. GLC–MS comparison with authentic samples identified the products as (*Z*)- and (*E*)-1,2-diphenyl-1-methoxyethenes. Measurements to obtain deuterium incorporations are detailed in the text.

The contents of the cold trap (toluenes and some distilled DMSO) were thawed and CCl₄ (1 cm³) added by syringe. The solution was washed once with water, then filtered through alumina and added to a saturated solution of NO₂BF₄ in acetonitrile (1 cm³). After 30 min at room temperature, water (1 cm³) was added and the mixture shaken. The lower CCl₄ layer was pipetted out, filtered through silica, and retained for GLC–MS analysis. Comparison with authentic samples showed that the *o*-, *m*- and *p*-nitrotoluenes were formed in *ca.* 57:7:26 ratio. We found that there was some isotopic resolution occurring in the GC separations, with the early part of a peak associated with either the *ortho*- or *para*-isomer being enriched in deuteriated material. For measurement of deuterium incorporation in a particular isomer, ion intensities were integrated over the complete GC peak from that isomer. Isotopic incorporations in the mixture were then determined from relative peak intensities in the group associated with the ion by standard methods.⁴⁸ The incorporations were accepted only if the sum of isotopomers was 100.0 (±1.0)%. Results are detailed in the text.

¹H NMR Monitoring of the Fragmentation.—These experiments were run on a Varian Gemini 200 spectrometer. The alcohol, **1a** or **1e** (0.003 g), was weighed accurately into a 5 mm NMR tube which was then mounted on the gas line and repeatedly evacuated and refilled with argon. [²H₆]-DMSO (0.25 cm³) was added by syringe and the alcohol dissolved. A solution of [²H₆]-dimethyl sodium in [²H₆]-DMSO (0.5 cm³; 0.09 mol dm^{–3}) was then added and the sample mixed by gentle shaking. Final concentrations were for the alcohol, 0.014 mol dm^{–3} and for base, 0.064 mol dm^{–3}. The tube was then sealed and transferred to the probe of the spectrometer so that the first spectrum was run *ca.* 8 min after mixing with a pulse width of 14.7 μ s (15° pulse), acquisition time of 2.666 s and delay of 3.00 s. The probe temperature was a nominal 21.0 ± 0.1 °C during the experiment. The alkoxide shows signals at δ 2.83 (2 H, d, *J* 14.3), 3.14 (2 H, d, *J* 14.3), 6.8 to 7.4 (13 H, m) and 7.48 (2 H, d, *J* 10). The enolate shows signals at 5.71 (1 H, s), 6.86 (1 H, t, *J* 7.5), 7.32 (2 H, t, *J* 7.5), 7.51 (3 H, m), 8.11 (2 H, d, *J* 7.5) and 8.18 (2 H, d, *J* 7.5).

* C. F. H. Allen and W. E. Barker, *Org. Synth.*, 1943, Coll. Vol. 2, 156.

Kinetic Isotope Effect Measurements on 1a and 1b.—For the measurements by UV spectroscopy, the reaction vessel was a water-jacketed cell fitted with a stirrer and a fibre-optic probe from a Guided-Wave Model 200 UV-VIS spectrometer. The vessel was mounted on a vacuum line and water at 30.4 (± 0.1) °C was circulated through the jacket. The cell was evacuated then filled with argon at least three times before dry DMSO (4.5 cm³) was added by syringe followed by dimethyl sodium solution (2.5 cm³; 0.099 mol dm⁻³). The stirred solution was allowed to equilibrate to temperature for at least 15 min, then a solution of the alcohol, **1a** or **1b**, in DMSO (0.05 cm³; 0.007 mol dm⁻³) was added in *ca.* 2 s by syringe. Reaction was timed from beginning of the addition and change in absorbance at 395 nm monitored at appropriate intervals over at least five reaction half-lives. First-order rate constants were extracted using a non-linear least-squares fitting procedure.

For the rate measurements for comparison of **1a** and **1b**, equal amounts (*ca.* 0.005 g) were accurately weighed into an NMR tube which was then attached to a gas line and placed under an argon atmosphere. DMSO (0.50 cm³) was then added and the alcohols were dissolved and the solution thoroughly mixed. As quickly as possible, [²H₆]-dimethyl sodium solution (0.25 cm³ of 0.27 mol dm⁻³) was then added by syringe, the solution mixed and the tube sealed. Final concentrations for alcohol and base were 0.090 and 0.049 mol dm⁻³, respectively. The reaction was timed from the mixing of the added dimethyl sodium solution. The tube was then transferred to the probe of an AC 300 spectrometer and spectra recorded at appropriate time intervals. Probe temperatures were stable at 21 \pm 0.5 °C throughout the experiment. Rates were determined first by non-linear least-squares fit of a single exponential to the growth of the alkene hydrogen signal to yield a value for the H-isotopomer, **1a**. Growth of the aromatic signal (δ 6.89) then yielded a value for **1b** by using the sum of the two exponentials^{4,9} with contributions in the ratio of the known mole fraction of **1a** and **1b** to fit to the data, with the previously determined constant for **1a** as a fixed constant for one of the curves.

Negative Ion Gas-phase Fragmentations.—These experiments were run on a Kratos Concept LS double-focusing mass spectrometer, using a standard CI source which was maintained at 80 °C. Argon was the bath gas, and the reagent gas, butyl nitrite, was conveniently introduced into the source *via* the GC inlet through a 1 m capillary tube from the head space of a vial of the liquid reagent maintained at 25 °C. Pressure in the source was between 10⁻¹ and 10⁻² Torr.* The sample was introduced as a solid and volatilized by raising the probe temperature to 80 °C. Under these conditions, standard spectra showed peaks at *m/z* = 287 (25%), 196 (100), from the triphenylpropanol, and at 73 and 147 from BuO⁻ and its hydrogen-bonded dimer. *B/E* linked scans were used to monitor daughters of parent at *m/z* = 287 (in the case of **1a**) or the appropriate parent in the case of the isotopomers. Slit width in the second field free region was 2 μ m in these experiments. Isotope effects were measured as relative peak areas of metastable ions.

Computational Studies.—The BEBOVIB-IV programme of Sims and his co-workers was run on a SUN microsystems SPARC workstation after minor modification to the Fortran code. In reactant models, all bonds were assumed to be normal with bond orders *n* = 1. For the transition state models, reacting bond lengths were adjusted using the Pauling relationship:

$$r = r_0 - 0.3 \ln(n)$$

A simple valence force field was used for both reactant and transition state models, with the exception of the off-diagonal elements necessary to generate the reaction coordinate frequency in the TS. Bond lengths, angles and reactant force constants were standard values recommended for use with BEBOVIB-IV and TS force constants were calculated from bond orders through the empirical relations which are the basis of the BEBO method. Stretching constants for the bond between atoms *i* and *j* were given by:

$$F_{ij} = n_{ij} F_{ij}^\circ$$

Bending for the angle at atom *j* between atoms *i*, *j* and *k* was given by:

$$F_\alpha = g_\alpha (n_{ij} n_{jk})^{\frac{1}{2}} F_\alpha^\circ$$

where F_{ij}° and F_α° are the standard force constants, n_{ij} is the Pauling bond order for the bond *ij* and g_α is an empirical geometry factor given by:

$$g_\alpha = 1.389 + 1.167 \cos \alpha$$

The reaction coordinate was generated by coupling the bond-stretches of the breaking C–C bond and the C–O bond which develops from single to double as the reaction progresses. A coupling constant of 1.1 yielded the tabulated values of the imaginary frequency. Tunnel corrections were always less than 2% of the semi-classical effects.

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* 1 Torr = *ca.* 133.322 Pa.

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