

Figure 2. UV/vis and ESR spectra of $1^{\bullet-}$ ($a_H = 1.25$ G) and $2^{\bullet-}$ ($a_H = 2.73$ G) in THF/HMPA (10% v/v) at -90 °C (K^+ as the counterion). The spectra presented were obtained under identical conditions¹⁴ by reduction of **1** and **2** with identical amounts of the reducing agent (K^+ , biphenyl⁻). The bands at 354 nm ($1^{\bullet-}$) and 338 nm ($2^{\bullet-}$) are assigned to the $\pi \rightarrow \pi^*$ transitions.

tetraone **1** were susceptible to nucleophilic attack that resulted in a series of rearrangements,¹¹ forcing us to carry out the radical anion experiments at low temperatures (see below).

The crucial information about the LUMO in **1** was provided by the measurement of reduction potentials¹³ of **1** (-0.90 V) and the appropriate model ketones, **4** (-1.51 V) and **5** (-1.36 V). The addition of a carbonyl group to **4** lowered its reduction potential by 0.15 V. Thus, if the effect was purely additive the estimated reduction potential of **1** should have been -1.21 V, instead of the observed -0.90 V. These results indicate a lowering of the LUMO in **1** by 0.31 eV in comparison to a hypothetical nonspiroconjugated model.¹⁰

The radical anions of **1** and the half-molecule model, **2**, were prepared¹⁴ at low temperature (195–173 K) in THF/HMPA (10% v/v) mixtures with radical anions of polycyclic aromatic compounds serving as electron donors. Figure 2 shows the UV/visible and ESR spectra of potassium salts of $1^{\bullet-}$ and $2^{\bullet-}$ recorded under identical conditions. The pale yellow solution of $2^{\bullet-}$ showed the characteristic three-line spectrum¹⁵ resulting from the coupling to C-5 and C-6 protons. The ESR spectrum of the orange solution of $1^{\bullet-}$ showed five lines, indicating coupling to four equivalent hydrogens. Both ESR spectra are in qualitative agreement with the relative sizes of the LUMO coefficients (Figure 1) and clearly indicate delocalization of the unpaired spin density over the entire molecule in $1^{\bullet-}$, at least on the ESR time scale. In THF/HMPA the ESR spectra were independent of the counterion (Li^+ , Na^+ , and K^+), thus excluding any ion-pairing complications.

The distinction between simultaneous delocalization of the unpaired electron over the entire molecule of $1^{\bullet-}$ and a rapid

electron transfer (on the ESR time scale) between the halves can be obtained by UV/visible spectroscopy. In the latter case, the transitions between the highest doubly occupied MOs and the singly occupied MOs (intense $\pi \rightarrow \pi^*$ bands in Figure 2) in $1^{\bullet-}$ and $2^{\bullet-}$ should be of identical energy and intensity. The spectra of these anions obtained in THF/HMPA (10% v/v) were, however, quite different (Figure 2). In agreement with a spiroconjugated SOMO, the $\pi \rightarrow \pi^*$ band in the spectrum of $1^{\bullet-}$ is twice as intense as that in the spectrum of $2^{\bullet-}$ and shifted significantly toward longer wavelengths.¹⁶

The present results establish that the unpaired electron in $1^{\bullet-}$ is simultaneously delocalized over two perpendicular π -planes. To our knowledge, this is the first example of an organic spiroconjugated radical anion.^{8,17} The "three-dimensional" character of the LUMO in this acceptor should lead to CT interactions of increased dimensionality. New materials based on such interactions are currently being prepared in our laboratory.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society. P.M. is a recipient of the Camille and Henry Dreyfus Foundation New Faculty Award.

(16) There are two degenerate (or near-degenerate) highest doubly occupied MOs in **1**, but there is only one such orbital in **2**. Both compounds should have similar transition dipoles since they have similar frontier orbitals (Figure 1). Therefore, the probability of the $\pi \rightarrow \pi^*$ transition will double in $1^{\bullet-}$ as compared to $2^{\bullet-}$ (a model for a "localized" version of $1^{\bullet-}$). The bathochromic shift is due to the lowering of the SOMO in $1^{\bullet-}$ (ref 9). The weaker, longer wavelength bands correspond to $n \rightarrow \pi^*$ transitions (Figure 2). They are also bathochromically shifted. The neutral tetraone (**1**) also showed the effects of spiroconjugation in its UV/vis spectrum. In comparison to **2**, both the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions in the spectrum of **1** were more intense and bathochromically shifted. The extinction coefficients (in $M^{-1} cm^{-1}$) in CH_3CN for **1** are as follows: $\pi \rightarrow \pi^*$, $\epsilon_{236} = 83\,800$; $n \rightarrow \pi^*$, $\epsilon_{305} = 2300$; and $\epsilon_{344} = 900$. Analogous data for **2** (in $M^{-1} cm^{-1}$): $\pi \rightarrow \pi^*$, $\epsilon_{223} = 54\,600$; $n \rightarrow \pi^*$, $\epsilon_{300} = 700$; and $\epsilon_{344} = 120$.

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Extremely High Rate Accelerations in Aldol Reactions of α -Alkoxy Ketones: Reactivity Governed by Substituent Field Effects

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Received March 5, 1990

Aldol reactions play a major role in modern synthesis, yet little is known about structural effects on reactivity.¹⁻⁶ Consequently, we have targeted this area for study. We have discovered very large rate accelerations in aldol reactions of α -substituted ketones with the lithium enolate of pinacolone. Our results establish that (1) chelation is not responsible for these accelerations; (2) instead, a purely field/inductive (σ_I) effect is the major source of the high reactivities; and (3) the reactivity range is so large that it permits

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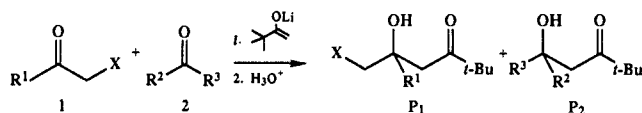
(14) ESR and UV/visible spectra were independent of the reducing agent used. The relative intensities of the UV/visible spectra of $1^{\bullet-}$ and $2^{\bullet-}$ were also reproducible, but the absolute extinction coefficients have not been determined yet. The ketones were recovered unchanged in ca. 85-95% yield (GC vs internal standard) if the solutions of radical anions were treated with dioxigen.

(15) A similar coupling pattern ($a_{H5,H6} = 2.6$ G) has been reported for $2^{\bullet-}$ in DMSO. The coupling to ortho hydrogens ($a_{H4,H7} = 0.1$ G) in this radical anion could be resolved only with difficulty: (a) Nelsen, S. F. *J. Org. Chem.* **1973**, *38*, 2693. (b) Russell, G. A.; Blankespoor, R. L.; Mattox, J.; Whittle, P. R.; Symalla, D.; Dodd, J. R. *J. Am. Chem. Soc.* **1974**, *96*, 7249.

Table 1. Relative Reactivities for Aldol Reactions of Ketones with Pinacolone Lithium Enolate in Diethyl Ether at -78°C

ketone pair, 1/2	rel reactivities, k_1/k_2	
	relay ^a	direct ^b
MeCOMe/MeCOEt (1a/2a)		6.29 ± 0.39^c
MeCOCH ₂ N(Me) ₂ /MeCOEt (1b/2a)		14.3 ± 0.8^c
MeCOCH ₂ SMe/MeCOEt (1c/2a)		74.1 ± 2.4^c
MeCOCH ₂ OMe/MeCOEt (1d/2a)	374 ± 37^d	374 ± 37^c
MeCOCH ₂ OTBS/MeCOEt (1g/2a) ^e	798 ± 52^d	705 ± 14^c
MeCOCH ₂ Cl/MeCOEt (1e/2a)	9479 ± 310^d	
(MeOCH ₂) ₂ CO/MeCOEt (1f/2a)	$30\,712 \pm 1433^d$	
(MeOCH ₂) ₂ CO/BuCHO (1f/2b)		0.308 ± 0.028^d
THF-3-one/cyclopentanone (1i/2d) ^f	367 ± 60^d	432 ± 97^c
THP-3-one/cyclohexanone (1j/2e) ^g	378 ± 9^d	319 ± 25^c
cyclopentanone/MeCOEt (2d/2a)		0.587 ± 0.088^c
cyclohexanone/MeCOEt (2e/2a)	43.8 ± 1.4^d	
PhCOCH ₂ OMe/PhCOCH ₃ (1h/2c)		500 ± 101^d

^a Calculated by multiplication of independently measured ratios as $(k_1/k_{1e}) \times (k_{1e}/k_{2a})$, except $k_{1f}/k_{2a} = (k_{1f}/k_{1e}) \times (k_{1e}/k_{1c}) \times (k_{1c}/k_{2a})$.
^b Relative reactivities determined by direct measurement. ^c SD of at least three runs. ^d Average deviation of two runs. ^e OTBS = (*tert*-butyldimethylsilyl)oxy. ^f THF-3-one = 3-oxacyclopentanone. ^g THP-3-one = 3-oxacyclohexanone.

Scheme 1

useful regioselectivities for different α -substituted carbonyls, both acyclic and cyclic.

Chelation has been invoked to explain stereochemistry in certain aldol reactions of Li enolates, though not involving α -alkoxy carbonyl substrates,⁷⁻¹¹ but facial selectivities in aldol additions of Li (and Ti¹²) enolates to α -alkoxy aldehydes and ketones¹²⁻¹⁴ suggested predominantly Felkin-Anh¹⁵ transition structures and not chelated ones.

We have measured relative reactivities in aldol reactions of α -substituted ketones (Scheme 1; Table I),^{16,17} Ketones were advantageous because cyclic ones could be used to restrict transition-structure conformational possibilities. Kinetic controls established that the effects are entirely under kinetic, and not thermodynamic, control. Good agreement of data directly measured and calculated by relay shows that relative rates are not altered by the competing substrates present and that the data reflect true competitions, with no specific effects of substrate or products upon enolate complexation or aggregation properties.^{18,19} The relay data are more accurately measurable.

An α -alkoxy group gives very high accelerations relative to an α -CH₃ or α -CH₂ group for both acyclic and cyclic ketones. Since 3-oxacyclopentanone and 3-oxacyclohexanone,²⁰ in which the

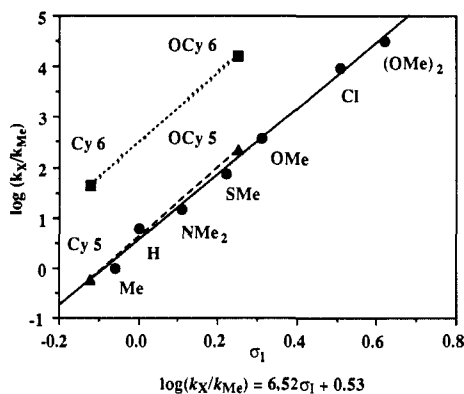


Figure 1. Plot of $\log(k_X/k_{Me})$ in diethyl ether at -78°C for 1a-f and 2a (rates with respect to k_{Me} , for butanone, 2a) against σ_1 .²⁴ For 1f, σ_1 was taken to be twice the σ_1 for OCH₃. Points for 1i, 1j, 2d, and 2e are shown (see text), but are not included in the least-squares fit. The sum of the σ_1 values for CH₃ and OCH₃ was used to approximate the net σ_1 appropriate for 1i and 1j; twice the σ_1 value for CH₃ was similarly used for 2d and 2e. OCy 6 = 3-oxacyclohexanone; OCy 5 = 3-oxacyclopentanone; Cy 6 = cyclohexanone; Cy 5 = cyclopentanone.

α -oxygens are held by the ring far from the carbonyl oxygen, exhibit accelerated rates almost identical with that of acyclic CH₃COCH₂OCH₃ (mean acceleration = $373 \pm$ only 1.5% for relay data), chelation cannot be the main source of the rate increases. This equality also shows that any rehybridization-related ring-strain changes^{21,22} have minimal effects upon the relative reactivities of 1i and 1j. The strong acceleration produced by a second methoxy group relative to a single one (Table I)²³ confirms nonchelation, which could only involve one α -alkoxy group at a time. Even though chelation is accessible with acyclic α -alkoxy ketones, where an eclipsed conformation of the C—O and C=O bonds can be attained, it does not serve to alter the reactivity by a significant amount.

We discovered (Figure 1) that $\log(k_X/k_{Me})$ correlates extremely well with σ_1 ²⁴ for substituents X ($\rho = 6.52$, $r = 0.996$), over a range of more than 4 orders of magnitude, but not with group electronegativities²⁵ or C=O π^* energies²⁶ (see supplementary material) or expected chelation order.²⁷ The large ρ value shows that rates are overwhelmingly controlled by electrostatic interactions in the low-polarity medium ether. Based on σ_1 additivity,²⁸ disubstituted ketones, even cyclopentanone and 3-oxacyclopentanone, fall very close to the correlation line. Dimethoxyacetone, though a ketone, is almost as reactive as valeraldehyde! Cyclohexanone and 3-oxacyclohexanone are both more reactive than other ketones, as expected,^{21,22} but the ρ value for these two points alone is similar to that found for acyclic ketones. A field-type (σ_1) electrical effect^{25a} is clearly the major source of these reactivity effects, with little steric interference by α -substituents.

The absence of significant steric effects and the nonaberrant behavior of the relatively flat cyclopentanone and 3-oxacyclopentanone are best explained by similar transition structures for both cyclic and acyclic substrates, with X—C—C=O dihedral angles similar to those in the five- or six-membered rings, i.e.,

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approaching 180°, as in the Cram²⁹ and Cornforth³⁰ models. Transition structures approaching Felkin-Anh geometry may also be conceivable since σ_1 effects may not be highly angle-sensitive.³¹

Although aldol reactions are known to proceed through complex aggregated species^{18,32} where enolate-aldolate species also sometimes dictate the stereochemical outcome,³³ our rate effects depend almost exclusively on substituent field/inductive parameters. Mechanistically, these results make clear that observed nonchelation facial selectivities in aldol reactions of α -alkoxy aldehydes and ketones¹²⁻¹⁴ result at least in part from very high acceleration of the nonchelation mechanism by α -alkoxy substituents, not just from an inefficient chelation mechanism! The large magnitude of these rate enhancements (Cl \gg OR $>$ SR \gg Me) makes α -heteroatomic substitution a very useful synthetic strategy for regioselective intramolecular competitions. Experiments are in progress to determine the nature of the interactions in α -chiral systems, whether observed stereochemistries which are consistent with chelation control truly result from chelation mechanisms, and whether chelation can be made operative under different experimental conditions.

Acknowledgment. We thank Dr. George Furst, NMR Facility, and Dr. John Dykins, Mass Spectrometry Facility, for their splendid assistance. Support by the National Institutes of Health and for equipment by the University of Pennsylvania Research Fund is gratefully acknowledged.

Supplementary Material Available: Plots of $\log(k_X/k_{Me})$ vs electronegativity parameters and π^* orbital energies (2 pages). Ordering information is given on any current masthead page.

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Radical Ion Probes. 1. Cyclopropylcarbinyl Rearrangements of Aryl Cyclopropyl Ketyl Anions

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Received February 5, 1990

A popular approach for the experimental detection of electron-transfer pathways in organic reactions involves the use of intramolecular rearrangements. If an appropriate structural probe is incorporated into the substrate, the intermediacy of a radical or radical ion can often be inferred by the appearance of rearranged products. For free radicals, these rearrangement processes are well-documented,^{1,2} and in several cases, their absolute rate constants are known.³ In the case of radical ions, however, it is often assumed implicitly that the same structural features will also lead to rearrangement. This notion is based upon the precept that the driving force for rearrangement of a radical and a radical

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Scheme 1

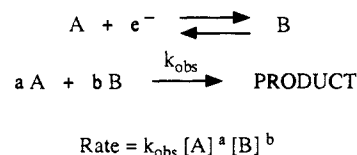


Table I. Summary of Data Pertaining to the Electrochemical Reduction of Phenyl Cyclopropyl Ketones 1 → 4

compd	$E_{1/2}^a$ vs Ag/Ag ⁺ , V	$R_{A/B}^b$	$\delta E_p/\delta \log(\nu)^c$, mV/decade	$\delta E_p/\delta \log(C_A)^d$, mV/decade	k_{obs}^e , M ⁻¹ s ⁻¹	E_a^f , kcal/mol
1	-2.420	2.0	<i>g</i>	<i>g</i>	4.5	10.2
2	-2.435	1.7	<i>g</i>	<i>g</i>	13.1	8.3
3	-2.435	1.9	-17.3	19.4	180.	7.4
4	-2.24 ^h	<i>i</i>	-33.4	4.2	<i>i</i>	<i>i</i>

^aAll experiments were carried out at a planar gold electrode in DMF with *n*-Bu₄NBF₄ as supporting electrolyte; Ag/Ag⁺ (0.1 M in CH₃CN) reference. ^b $R_{A/B} = [\delta \log(\nu_C)/\delta \log(C_A)] + 1$, determined by derivative cyclic voltammetry (see text). ^cVariation in peak potential (E_p) as a function of sweep rate, determined by linear sweep voltammetry. ^dVariation in peak potential (E_p) as a function of substrate concentration (C_A), determined by linear sweep voltammetry. ^eOverall rate constant at 20 °C, determined by $k(\text{EC}_{\text{DIM}}) = 0.1173(F/RT)\nu_{0.5}/C_A$ (refs 21 and 22) and digital simulation (refs 31 and 32). ^fApparent activation energy, determined by observing the effect of temperature on ν_C and fitting $\ln(1/\nu_C) = (-E_a/R)(1/T) + C$ (refs 21 and 22). ^gReaction kinetics too slow for LSV analysis. ^hPeak potential at 50 mV/s; no anodic wave observed. ⁱReaction kinetics too fast for DCV analysis.

Table II. Theoretical LSV Response for a First-Order and a Second-Order Radical Anion Decay^a

rate law	$\delta E_p/\delta \log(\nu)^a$, mV/decade	$\delta E_p/\delta \log(C_A)^b$, mV/decade
$k_{\text{obs}}[B]$	-29.5	0.0
$k_{\text{obs}}[B]^2$	-19.7	19.7

^a $-\delta E_p/\delta \log(\nu) = 1/(1+b)[\ln(10)](RT/nF)$ where b is the reaction order in B (refs 21 and 22 and Scheme 1). ^b $-\delta E_p/\delta \log(C_A) = (a+b-1)/(b+1)[\ln(10)](RT/nF)$, where a and b are the reaction orders in A and B, respectively (refs 21 and 22 and Scheme 1).

ion are likely to be quite similar. In this communication, we provide evidence that demonstrates that while this assumption may be valid, these radical ion probes have not yet reached the level of reliability of their free radical counterparts, and consequently, extreme caution should be exercised in their use as diagnostic probes in mechanistic studies.

Cyclopropylcarbinyl type rearrangements of ketyl anions have been utilized frequently in mechanistic studies.⁴⁻⁸ However, there are several conflicting reports in the literature regarding the integrity of a cyclopropyl ring in radical anions.^{4,9-18} Because of the disparity of these observations and because aryl cyclopropyl

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