

approaching 180°, as in the Cram²⁹ and Cornforth³⁰ models. Transition structures approaching Felkin-Anh geometry may also be conceivable since σ_I 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.

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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.

(29) Cram, D. J.; Abd Elhazef, F. A. *J. Am. Chem. Soc.* **1952**, *74*, 5828-5835.

(30) Cornforth, J. W.; Cornforth, R. H.; Mathew, K. K. *J. Chem. Soc.* **1959**, 112-127.

(31) As an approximation of the magnitude of the angular effect, charge-dipole and dipole-dipole interactions have a cosine dependence, which requires a deviation of over 25° from 180° to alter the interaction by 10%; Hine, J. *Structural Effects on Equilibria in Organic Chemistry*; Robert E. Krieger Publishing Co.: Huntington, NY, 1981; p 30.

(32) Williard, P. G.; MacEwan, G. J. *J. Am. Chem. Soc.* **1989**, *111*, 7671-7672.

(33) Alberts, A. H.; Wynberg, H. *J. Am. Chem. Soc.* **1989**, *111*, 7265-7266.

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

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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

(1) Wilt, J. W. In *Free Radicals, Vol. 1*; Kochi, J. K., Ed., Wiley: New York, 1973; pp 334-501.

(2) Beckwith, A. L. J.; Ingold, K. U. In *Rearrangements in Ground and Excited States, Vol. 1*; DeMayo, P., Ed.; Academic Press: New York, 1980; pp 161-310.

(3) Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1980**, *13*, 317.

Scheme I

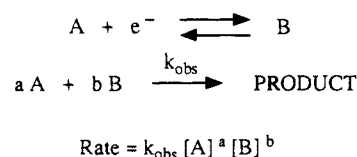


Table I. Summary of Data Pertaining to the Electrochemical Reduction of Phenyl Cyclopropyl Ketones 1 → 4

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 I). ^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 I).

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

(4) House, H. O.; Prabhu, A. V.; Wilkins, J. M.; Lee, L. F. *J. Org. Chem.* **1976**, *41*, 3067.

(5) House, H. O.; Weeks, P. D. *J. Am. Chem. Soc.* **1975**, *97*, 2778.

(6) Loots, M. J.; Dayrit, F. M.; Schwartz, J. *Bull. Soc. Chim. Belg.* **1980**, *89*, 897.

(7) Tanner, D. D.; Diaz, G. E.; Potter, A. *J. Org. Chem.* **1985**, *50*, 2149.

(8) Yang, D.; Tanner, D. D. *J. Org. Chem.* **1986**, *51*, 2267.

(9) Volkenburgh, R. V.; Greenlee, K. W.; Derfer, J. M.; Boord, C. E. *J. Am. Chem. Soc.* **1949**, *71*, 3595.

(10) Norin, T. *Acta Chem. Scand.* **1965**, *19*, 1289.

(11) Dauben, W. G.; Deviny, E. J. *J. Org. Chem.* **1966**, *31*, 3794.

(12) Russell, G. A.; Malkus, H. *J. Am. Chem. Soc.* **1967**, *89*, 160.

(13) House, H. O.; Blankley, C. J. *J. Org. Chem.* **1968**, *33*, 47.

(14) Fraisse-Jullien, R.; Frejaville, C. *Bull. Soc. Chim. Fr.* **1968**, 4449.

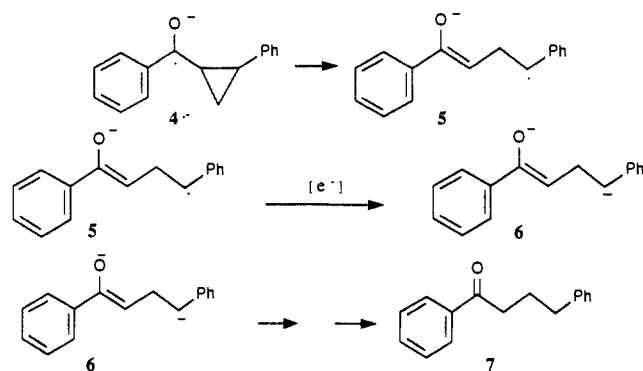
(15) Dauben, W. G.; Wolf, R. E. *J. Org. Chem.* **1970**, *35*, 374.

(16) Shiota, H.; Ohkata, K.; Hanafusa, T. *Chem. Lett.* **1974**, 1153.

(17) Mandell, L.; Johnston, J. C.; Day, R. A., Jr. *J. Org. Chem.* **1978**, *43*, 1616.

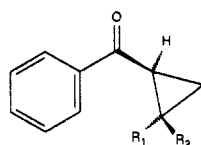
(18) Mairanovskii, S. G.; Kosycheno, L. I.; Kuryavtseva, G. A.; Kudryavtsev, R. V. *Elektrokhimiya* **1979**, *15*, 1240; *Chem. Abstr.* **1979**, *91*, 192493m.

Scheme II



ketones (in particular) have been utilized in several mechanistic studies, we began a detailed study of the chemistry of their corresponding ketyl anions.¹⁹

Utilizing derivative cyclic voltammetry (DCV), we examined the mechanisms of the electrochemical reduction of 1-4. For a reversible electrochemical process coupled with rate-limiting homogeneous kinetics (Scheme I), the "reaction-order approach", reviewed extensively by Parker,²⁰⁻²² provides a means of assessing the rate law for radical anion decay. In the DCV experiments, the anodic/cathodic derivative current ratio (R_{DCV}) was the observable.

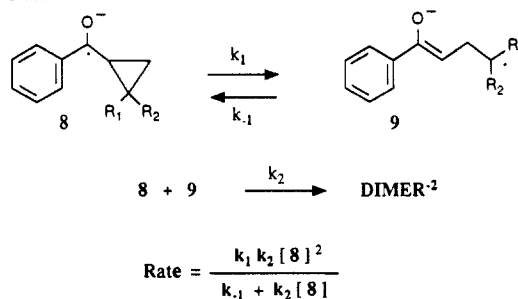


- 1 ($R_1 = R_2 = H$)
- 2 ($R_1 = CH_3; R_2 = H$)
- 3 ($R_1 = R_2 = CH_3$)
- 4 ($R_1 = Ph; R_2 = H$)

At several concentrations of substrate, the sweep rate (ν) was adjusted to keep R_{DCV} constant. A plot of $\log(\nu_C)$ vs $\log(C_A)$ yields a straight line whose slope is related to the combined reaction order in A and B: $R_{A/B} = 1 + [\delta \log(\nu_C) / \delta \log(C_A)]$.^{21,22} Deconvolution of the individual reaction orders in A and B was accomplished via linear sweep voltammetry (LSV). The results appear in Table I. Theoretical data for first- and second-order radical ion decay are summarized in Table II.^{21,22}

The only system found to be first order in radical anion was 4. Controlled-potential coulometry yielded 1,4-diphenyl-1-butanone (7) as the only observed product (66% yield with 17% recovered starting material) with the net consumption of 2 faradays of electricity.²³ These results are consistent with the mechanism presented in Scheme II: cyclopropylcarbinyl ring opening of 4⁻, followed by rapid reduction of the ring-opened distonic radical anion 5.²⁴ Because the conversion 4⁻ → 5 is the rate-determining step, it is impossible to assess whether the *second* electron-transfer step is heterogeneous (ECE, 5 + e⁻ → 6) or homogeneous (ECE_h, 4⁻ + 5 → 4 + 6).²⁵⁻²⁷

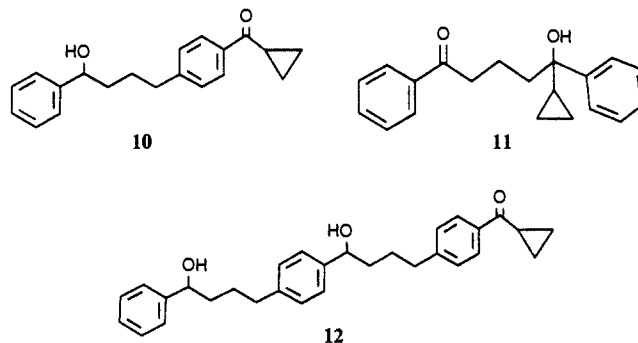
Scheme III



In contrast, 1⁻, 2⁻, and 3⁻ exhibit *second-order* decay. Furthermore, increased alkyl substitution *increases* the apparent rate of decay of the radical anion, 3⁻ > 2⁻ > 1⁻, suggesting that electronic rather than steric factors govern the rate. For systems without the cyclopropyl group, which decay by a dimerization mechanism (e.g., 2Ph(C=O⁻)R → (DIMER)²⁻),²⁸⁻³⁰ steric effects *are* important and we observe an opposite trend: R = CH₃ > CH₂CH₃ >> CH(CH₃)₂ > C(CH₃)₃.

These observations are completely explained by the mechanism presented in Scheme III: Radical anion 8 ring-opens *reversibly* to distonic radical anion 9, which is subsequently trapped by ring-closed species 8. The composite rate constant for this reaction (k_{obsd}) reduces to $(k_1/k_{-1})k_2$, assuming that the second step is rate determining. Rate constants (k_{obsd}) and activation energies were determined for 1-3 (Table I). It is important to note that the relative magnitudes of k_1 , k_{-1} , and k_2 are unknown at this time.

Controlled-current electrolysis of 1 (1 Faraday electricity) yielded 14% recovered starting material, dimers 10 and 11 in 41 and 7% yields, respectively, and trimer 12 (11%). Similar products were also obtained for the reduction of 2 and 3.



In conclusion, aryl cyclopropyl ketyl anions whose only substituents on the cyclopropyl ring are alkyl or hydrogen undergo a *reversible* ring-opening process. The consequence of these results for mechanistic studies is clear: Because the ring opening is reversible, these substrates are unreliable probes for electron-transfer processes.

Acknowledgment. We gratefully acknowledge the Department of Chemistry at Virginia Tech and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support. R.E.D. expresses sincere gratitude to Mobay Chemical Corporation for a tuition fellowship for the 1989-1990 academic year.

(19) For a review of cyclopropyl ketone electrochemistry, see: Becker, J. Y. In *The Chemistry of the Cyclopropyl Group*; Rappoport, Z., Wiley: New York, 1987; pp 915-958.

(20) Parker, V. D. In *Topics in Organic Electrochemistry*; Fry, A. J., Britton, W. E., Eds.; Plenum Press: New York, 1986; pp 35-79.

(21) Parker, V. D. In *Advances in Physical Organic Chemistry*, Vol. 19; Gold, V., Bethell, D., Eds.; Academic Press: New York, 1983; pp 131-223.

(22) Parker, V. D. *Electroanal. Chem.* **1986**, *14*, 1.

(23) Similar results were reported by Mandell et al. (ref 17) in aqueous solution.

(24) The reduction potential of benzyl radical (-1.77 V vs Ag/Ag⁺ (0.1 M)) is considerably more positive than that of 1-benzoyl-2-phenylcyclopropane (4), consistent with the second reduction step proposed in Scheme II. Wayner, D. D. M.; McPhee, D. J.; Griller, D. *J. Am. Chem. Soc.* **1988**, *110*, 132.

(25) Amatore, C.; Saveant, J. M. *J. Electroanal. Chem.* **1977**, *85*, 27.

(26) Amatore, C.; Saveant, J. M. *J. Electroanal. Chem.* **1978**, *86*, 227.

(27) A referee has suggested an alternative ECE_h mechanism involving protonation of 5 followed by rapid reduction by 4⁻.

(28) Bewick, A.; Brown, D. *J. Chem. Soc., Perkin Trans. 2* **1977**, 99.

(29) van Tilborg, W. J. M.; Smit, C. *J. Recl. Trav. Chim. Pays-Bas* **1979**, *98*, 532.

(30) Egashira, N.; Minami, T.; Kondo, T.; Hori, F. *Electrochim. Acta*, **1986**, *31*, 463.

(31) Britz, D. *Digital Simulation in Electrochemistry*; Springer-Verlag: New York, 1981.

(32) Maloy, J. T. In *Laboratory Techniques in Electroanalytical Chemistry*; Kissinger, P. T., Heineman, W. R., Eds.; Marcel Dekker: New York, 1984; pp 417-461.