of a catalyst, tetrakis[4-*N*-methylpyridyl or 4-pyridyl]porphinecobalt(III) (Co^{III}TMPyP or Co^{III}TPyP), either dissolved in the solution or strongly adsorbed[1,2] on a glassy carbon or graphite electrode. Such a catalytic cathode in a divided cell (glass frit or NaFion membrane) produced H_2O_2 with an average yield of 93.7 ± 2.2% from an air-saturated 0.05 M H_2SO_4 catholyte. Values of E_{cat} between −0.1 and +0.2 V (referenced to a saturated KCl silver–silver chloride electrode) were employed. The amount of H_2O_2 produced was quantitated by titration with $KMnO_4$.[3]

The oxidation of I^- to I_2 illustrates the matching of the cathode and anode to produce the same product with 200% yield. The anolyte contained 0.5 M H_2SO_4 and 0.1 M KI. The H_2O_2 was generated catalytically from air-saturated H_2SO_4 and was then was reacted with an excess of KI. The I_2 formed was quantitated by titration with thiosulfate.[4] An average yield for I_2 was 194 ± 3% (anode, 101 ± 1%; cathode; 93 ± 3%). Br_2 could be similarly generated from Br^-. Yields were independent of the applied cathodic potential between −0.2 and +0.2 V. When the potential became more negative than −0.20 V, the yield decreased, possibly due to H_2O_2 reduction at the cathode.

Two different electrosynthetic conversions, As(III) to As(V) and the bromination of cyclohexene, were attempted, each relying on the ability to generate I_2 or Br_2 as a reagent. Since the oxidation of As(III) is electrochemically irreversible at most electrodes,[5-7] it was accomplished indirectly through the generation of Br_2 (or I_2) at the anode and H_2O_2 catalytically at the cathode. The average total yield of As(V) was 155 ± 5% (anode, 95 ± 1%; cathode, 60 ± 5%). The catholyte contained 0.02 M $HAsO_2$ in 0.5 M H_2SO_4, and the anolyte 0.02 M $HAsO_2$ in 0.5 M H_2SO_4 and 0.4 M KBr. The charge passed through the cell varied from 20 to 45 C for each run. The yield was determined by analyzing for the unreacted As(III) remaining by iodometric titration.[8] The presence of As(V) has no effect on the yield while the addition of KBr (0.4 and 1.3 M) to the cathodic compartment increased the yield (cathode, 77% and 89%, respectively). This increase is believed to be due to the H_2O_2, which, besides oxidizing As(III) to As(V), also oxidizes Br^- to Br_2, which in turn oxidizes As(III). Although the rate for the reaction between H_2O_2 and Br^- is relatively slow,[9] the large excess of Br^- competes favorably to circumvent the loss of H_2O_2 through disproportionation. Thus, yields approaching 200% appear feasible.

In the case of cyclohexane bromination, it was necessary to transfer the Br_2 generated in both compartments to an external reaction vessel containing cyclohexene. This transfer was made by passing an air stream through the anolyte during electrolysis. In the catholyte (0.5 M H_2SO_4) O_2 was bubbled through the solution during electrolysis for conversion to H_2O_2, and solid KBr was added after the electrolysis was stopped. The Br_2 formed was then transferred via an air stream to a second external reactor containing cyclohexene dissolved in CCl_4 and maintained at ice temperature. After CCl_4 was evaporated, the residue was dissolved in ethanol and subjected to gas chromatographic analysis; 1% DMF in ethanol served as an internal reference. The average total yield of dibromocyclohexane was 148 ± 5% (anode, 87 ± 2%; cathode, 61 ± 6%). The lower cathodic yield may reflect a loss of H_2O_2 during the generation period and/or a lower efficiency of the H_2O_2–Br^- reaction rather than an inefficiency in the Br_2 transfer and reaction with cyclohexene. Nonetheless, the yield was significantly increased above a conventional cell utilizing only the anodic compartment.

There have been reports in which both anodic and cathodic reactions have been matched to yield a single product. For example, NaOH, generated from the cathodic compartment of a chlor-alkali cell, can be reacted with the anodically generated Cl_2 to produce sodium hypochlorite or, through further oxidation, sodium chlorate.[10] Two other "matched" electrosynthetic schemes have been also recently reported.[11,12] However, the matching of *both* cell compartments to produce the same product from a common reactant has not been previously reported or demonstrated. Experiments are underway to explore the full scope and applicability of the concept.

Acknowledgment. We gratefully acknowledge the support of this work by a grant from Koppers Co., Inc., Pittsburg, PA.

Registry No. H_2O_2, 7722-84-1; O_2, 7782-44-7; I^-, 7681-11-0; Br, 24959-67-9; Br_2, 7726-95-6; I_2, 7553-56-2; $HAsO_2$, 13768-07-5; H_3AsO_4, 7778-39-4; KBr, 7758-02-3; Co^{III}TMPgP, 51329-41-0; Co^{III}TPyP, 61136-56-9; cyclohexene, 110-83-8; dibromocyclohexane, 52590-61-1.

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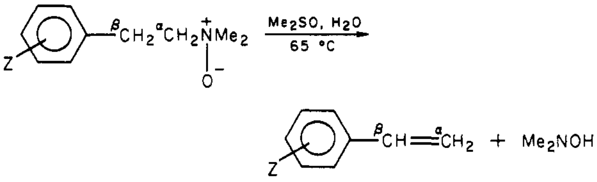
Carbon-14 Kinetic Isotope Effects and Kinetic Studies in the Syn-Elimination Reactions of (2-Phenylethyl)dimethylamine Oxides[1]

Daniel R. Wright, Leslie B. Sims, and Arthur Fry*

Department of Chemistry, University of Arkansas
Fayetteville, Arkansas 72701

Received January 24, 1983

As the first reported example of a carbon isotope effect in a clearly established syn-elimination reaction, we have found that there are large carbon-14 kinetic isotope effects in the thermal decomposition of both α- and β-carbon-14 labeled (2-phenylethyl)dimethylamine oxides (eq 1). The effects of substituents on the rates of the reactions for Z = *p*-CH_3O, *p*-CH_3, H, and *p*-Cl have also been investigated.



(1)

$$k/{}^{\alpha}k = 1.061 \pm 0.006 \qquad k/{}^{\beta}k = 1.036 \pm 0.005$$

All of the reaction systems for which carbon isotope effect data[2-4] have been reported to date[2] by our research group[3] and that of Saunders[4] have had E2 mechanisms with varying degrees

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(1) This work was supported by the National Science Foundation.

(2) Fry, A. *Chem. Soc. Rev.* **1972**, *1*, 163-210. References to earlier heavy-atom isotope effect studies of elimination reaction mechanisms are to be found in this review.

(3) For a current brief review of our experimental work, see: Fry, A.; Sims, L. B.; Eubanks, J. R. I.; Hasan, T.; Kanski, R.; Pettigrew, F. A.; Crook, S. "Proceedings of the International Symposium on the Synthesis of Appl. Isotopically Labeled Compounds"; Duncan, W. P., Susan, A. B., Eds.; Elsevier: Amsterdam, 1983; pp 133-138. Lewis, D. E.; Sims, L. B.; Yamataka, H.; McKenna, J. *J. Am. Chem. Soc.* **1980**, *102*, 7411-7419. Burton, G. W.; Sims, L. B.; McLennan, D. J. *J. Chem. Soc., Perkin Trans. 2* **1977**, 1847-1853. Hasan, T.; Sims, L. B.; Fry, A. *J. Am. Chem. Soc.*, in press. Eubanks, J. R. I. Ph.D. Dissertation, University of Arkansas, 1981. Pettigrew, F. A. Ph.D. Dissertation, University of Arkansas, 1981.

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Table I. Carbon-14 Kinetic Isotope Effects for the Thermolysis at 65 °C of (2-Phenylethyl-*1*-^{14}C)dimethylamine Oxide ($k/^{\alpha}k$) and (2-Phenylethyl-*2*-^{14}C)dimethylamine Oxide ($k/^{\beta}k$) in 10% Water–90% Dimethyl Sulfoxide

f	$k/^{\alpha}k$ from f, R_o, R_p	f	$k/^{\beta}k$ from R_o, R_r, R_p	f, R_o, R_p	f, R_o, R_r	f, R_r, R_p
0.0654	1.064	0.270	1.042	1.042	1.042	1.042
0.237	1.068	0.350	1.033	1.031	1.034	1.033
0.289	1.055	0.438	1.038	1.043	1.037	1.040
0.397	1.055	0.553	1.030	1.032	1.031	1.031
0.656	1.059	0.602	1.035	1.028	1.038	1.032
0.768	1.067	0.818			1.040	
av (±std dev)	1.061 (0.006)		1.036 (0.005)	1.036 (0.007)	1.037 (0.004)	1.036 (0.005)
			overall average for $k/^{\beta}k$, 1.036 ± 0.005			

of E1 or (mostly) E1cB character, and all have been thought to proceed entirely or mainly through anti-elimination pathways.[5]

The thermal decomposition of amine oxides,[6-9] sometimes known as the Cope reaction, is clearly an intramolecular[10,11] syn-elimination reaction as is well documented by several lines of stereochemical[12-14] and tracer[15] evidence.

The β-deuterium isotope effects in these reactions are small,[15-18] consistent with a nonlinear proton transfer in a cyclic five-membered ring syn-elimination transition state. However, in sharp contrast to their earlier temperature-independent work in diglyme,[17] Kwart's group later found[18] a substantial temperature dependence in the β-deuterium isotope effect for the thermolysis of *n*-heptyldimethylamine oxide in dimethyl sulfoxide. They interpreted[18] these results in terms of a linear proton transfer to the Me_2SO oxygen in a larger ring, where Me_2SO is coordinated with the amine oxide oxygen, and postulated that linearity vs. nonlinearity of proton transfer can be determined by temperature dependence vs. independence of the β-deuterium isotope effect.

Our program[19] of combining measured and calculated isotope effects for molecules successively labeled[20] at positions where bonding changes occur lends itself well to elucidating details of syn vs. anti mechanisms and controversial mechanistic questions such as ring size and linear vs. nonlinear proton transfers. The transition-state models for such processes are very different and will surely lead to different calculated isotope effect values.

A β-phenyl group clearly accelerates the decomposition of amine oxides,[21] but there are no literature reports on the relative reactivity of substituted 2-phenylethyl derivatives. A good linear Hammett relationship with $\rho = 0.77$[22] (correlation coefficient 0.988)[19] has been found[11] for thermolysis of substituted (1-phenylbutyl)dimethylamine oxides.

We have now measured the rates of decomposition of a series of substituted (2-phenylethyl)dimethylamine oxides in 10% water–90% Me_2SO at 65 °C. The kinetic data gave good first-order plots, and the rate constants, determined by least-squares methods, (substituent, $10^5 k_1 \pm$ standard deviation) are as follows: *p*-methoxy, 0.668 ± 0.054; *p*-methyl, 1.39 ± 0.18; H, 3.08 ± 0.69; *p*-chloro, 8.17 ± 1.19; *p*-nitro, too fast for convenient measurement. The Hammett plot of these data is reasonably linear (possibly concave downward) with $\rho = 2.11$ (correlation coefficient 0.994). Clearly, amine oxide decompositions are accelerated by electron-withdrawing groups at either C_α or C_β, indicating some buildup of negative charge at C_β and some decrease in the induced positive charge at C_α.

The $^{\alpha}C$ and $^{\beta}C$ carbon-14 labeled (2-phenylethyl)dimethylamine oxides were synthesized by conventional means[3,8] starting with sodium cyanide-^{14}C and benzoic-*7*-^{14}C acid, respectively.

The kinetic and isotope effect experiments were carried out at 65 °C in 10% water–90% dimethyl sulfoxide solution under a nitrogen atmosphere. For the isotope effect experiments, fractions of reaction, f, ranged from 7% to 82%. The radioactivity measurements were made on styrene dibromide samples prepared from the styrene formed at 100% reaction, R_o, at reaction fraction f, R_p, and after complete conversion of the recovered reactant to styrene, R_r. The isotope effects, $k/^{\alpha}k$ or $k/^{\beta}k$, reported in Table I were calculated[23] in four ways by using any three of the measured parameters, f, R_o, R_p, and R_r. Agreement of the results calculated in these four different ways and the lack of trends in the isotope effects at different values of f provide good evidence of the chemical and radiochemical purities of the reactants and of the satisfactory nature of the procedures used in making the measurements. For the α-labeled compounds, because of difficulties in handling the styrene, R_r measurements were unsatisfactory, and only the equation using f, R_o, and R_p was used. For the later β-labeling results all four equations gave good results.

The large (but different) isotope effects at the α, $k/^{\alpha}k = 1.061$, and β, $k/^{\beta}k = 1.036$, carbons in this syn thermolysis of (2-phenylethyl)dimethylamine oxide, may be compared to the corresponding values for the base-promoted anti elimination of trimethylamine from α- and β-labeled (2-phenylethyl)trimethylammonium bromides[3] at 40 °C, $k/^{\alpha}k = 1.044$ and $k/^{\beta}k = 1.040$. Both syn- and anti-elimination reactions have large isotope effects at both C_α and C_β, but clearly there is a greater bonding change at C_α in the amine oxide pyrolysis than in the quaternary ammonium salt decomposition. These data, combined with the Hammett plot data, give a picture of the transition state involving extensive rupture of both the C_α–N and C_β–H bonds, with rela-

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(19) For a recent example, see: Ando, T.; Kim, S.-G.; Matsuda, K. Yamataka, H.; Yukawa, Y.; Fry, A., Lewis, D. E.; Sims, L. B.; Wilson, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 3505–3516.

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(22) Three of the points in their[11] Figure 3b (Hammett plot) are mislabeled in the caption, but the correct values were used in the graph. They report, "the slope gives a value of ρ which is low and positive ($\rho \sim 2$)" whereas even a casual inspection of their graph shows that ρ is less than unity. Our least-squares calculation of ρ from their data gives the value of +0.77 reported here.

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tively little C_α–C_β double-bond character. The higher value of the ${}^{\alpha}C$ than the ${}^{\beta}C$ isotope effect is readily interpreted in terms of extensive delocalization of the developing negative charge at C_β into the aromatic ring (added C_β-ring bond formation).

Further experiments are planned to study the variation of the ${}^{\alpha}C$ and ${}^{\beta}C$ isotope effects with ring substituents and as the solvent is charged to the diglyme system, for which Kwart's group proposes a changeover from a linear (large ring–Me$_2$SO involved) β-proton transfer to a nonlinear transfer. Model calculations comparing syn and anti mechanisms and linear (Me$_2$SO involved) vs. nonlinear proton transfers are also planned. The carbon isotope effect data place stringent constraints on the structures and geometries of the acceptable transition-state models.

Acknowledgment. We are indebted to Drs. John R. I. Eubanks and M. Kanska for preparation of some of the labeled compounds.

Registry No. (2-(*p*-Methoxyphenyl)ethyl)dimethylamine *N*-oxide, 34875-26-8; (2-(*p*-methylphenyl)ethyl)dimethylamine *N*-oxide, 85662-27-7; (2-(*p*-chlorophenyl)ethyl)dimethylamine *N*-oxide, 34875-27-9; (2-phenylethyl)dimethylamine *N*-oxide, 19270-13-4; (2-(*p*-nitrophenyl)-ethyl)dimethylamino *N*-oxide, 85662-28-8; carbon-14, 14762-75-5.

Mild Lewis Acid Catalysis: Eu(fod)$_3$-Mediated Hetero-Diels-Alder Reaction

M. Bednarski and S. Danishefsky*

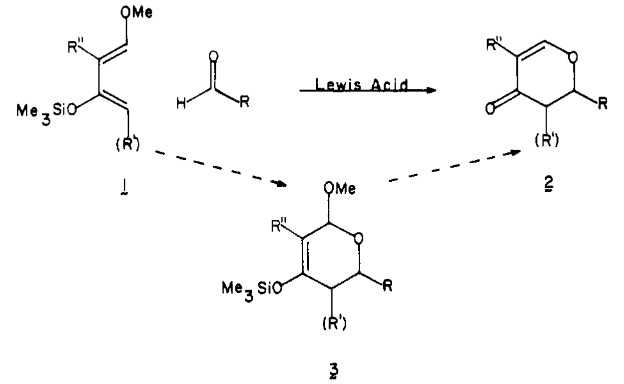
Department of Chemistry, Yale University
New Haven, Connecticut 06511

Received January 17, 1983

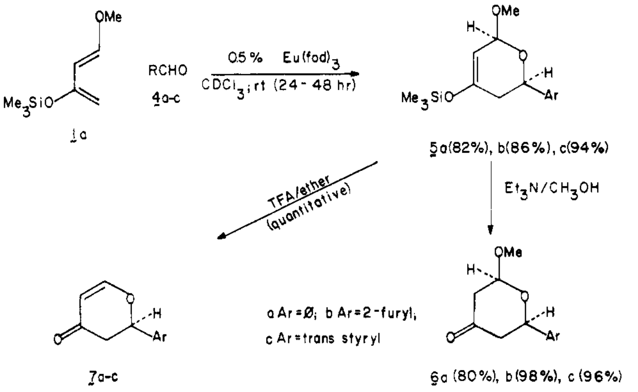
Under Lewis acid catalysis, cyclocondensations of dienes (cf. **1**, Scheme I) with aldehydes afford dihydropyrones (**2**). This process has been explored as to scope,[1,2] applications,[3] and mechanism.[4] Initially, the intermediacy of cycloadducts was presumed but not demonstrated. More recently, as part of our mechanistic investigations the acid-labile intermediates, **3**, could be detected and even isolated in modest yield.

There occurred to one of us the notion that the oxaphilicity of rare-earth cations,[5] suitably complexed with solubilizing ligands,[6] might so perturb an aldehyde[7,8] as to render it a potent heterodienophile. In this communication we report on the experimental realization of this hypothesis, using trace amounts of tris-(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato)europium (Eu(fod)$_3$) as the catalyst.

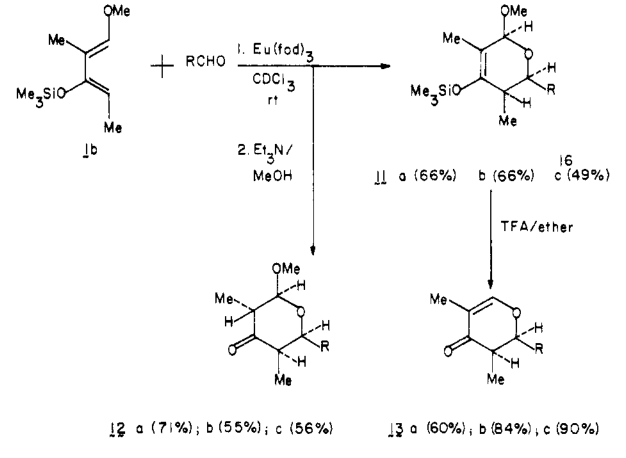
Scheme I



Scheme II



Scheme III



Our findings, using diene **1a** (Scheme II) with aromatic aldehydes, are provided below. With these substrates the *cis*[9]-methyl glycosides **5** were produced with good selectivity.[10] With a high

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(1) Danishefsky, S.; Larson, E. R.; Askin, D. *J. Am. Chem. Soc.* **1982**, *104*, 6457 and references therein.

(2) For thermal cycloadditions to activated (cf. glyoxalate, chloral, etc.) aldehydes see ref 1, footnotes 6–10. For some recent findings from other laboratories that have followed our disclosures see: (a) Belanger, J.; Landry, N. T.; Pare, R. J.; Jankowski, K. *J. Org. Chem.* **1982**, *47*, 3649. (c) Aben, R. W.; Scheeren, H. W. *Synthesis* **1982**, 779. (c) Brady, W. T.; Agho, M. O. *Ibid.* **1982**, 500.

(3) (a) Danishefsky, S.; Kato, N.; Askin, D.; Kerwin, J. F., Jr. *J. Am. Chem. Soc.* **1982**, *104*, 360. (b) Danishefsky, S.; Kerwin, J. F., Jr. *Ibid.* **1982**, 3183 and references therein.

(4) (a) Larson, E. R.; Danishefsky, S. *Tetrahedron Lett.* **1982**, *23*, 1975. (b) Larson, E. R.; Danishefsky, S. *J. Am. Chem. Soc.* **1982**, *104*, 6458.

(5) For recent discussions of the coordination properties of various lanthanides see: (a) Rueben, J. In "Handbook on the Physics and Chemistry of Rare Earths"; Gschneidner, K. A., Jr., Eyring, L., Eds.; North-Holland: Amsterdam, 1979; Chapter 39. (b) Richardson, F. S. *Chem. Rev.* **1982**, *82*, 541. (c) Marks, T. J. *Prog. Inorg. Chem.* **1978**, *24*, 51.

(6) In selecting ligands for the lanthanide in this and related ongoing investigations, we were influenced by considerations of demonstrated efficacy as NMR shift reagents; see: (a) Dyer, D. S.; Cunningham, J. A.; Brooks, J. J.; Sievers, R. E.; Rondeau, R. E. In "Nuclear Magnetic Resonance Shift Reagents"; Academic Press: New York, 1973; Chapter 2. (b) McCreary, M. D.; Lewis, D. W.; Wernick, D. L.; Whitesides, G. M. *J. Aam. Chem. Soc.* **1974**, *96*, 1038. The uses of other ligands are under investigation.

(7) To the best of our knowledge the concept and findings described here are novel. For previous apparent manifestations of the Lewis acidity of lanthanides in reactions of carbonyl compounds see: Trost, B. M.; Bogdonowicz, M. J. *J. Am. Chem. Soc.* **1973**, *95*, 2040. Luche, J. L.; Gemal, A. L. *J. Chem. Soc., Chem. Commun.* **1978**, 976. Forsberg, J. H.; Belasubramanian, T.; Spaziano, V. T. *Ibid.* **1976**, 1060. For a very recent listing of the applications of lanthanides in catalysis see: Marks, T. J.; Ernst, R. D. "Comprehensive Organometallic Chemistry", in press. We thank Professor Marks for providing us with a preprint of this valuable compilation.

(8) For the use of divalent lanthanides as reducing agents see: Natale, N. R. *Tetrahedron Lett.* **1982**, *23*, 5009.

(9) The stereochemical assignment of the pseudoglycal ethers, **5a–c** is best determined by their conversion to the β-methoxy ketones, **6a–c**, respectively. In the NMR spectra of the cis compounds **6a** and **6b**, the anomeric (C_1) proton appears as an apparent triplet, J-7-8 Hz, while the C_5 methine appears as a doublet of doublets $J_1 \simeq$ 11-12 Hz, $J_2 \simeq$ 2-3 Hz, implying an axial-like disposition for both of these hydrogens. The assignment of configuration at C_5 in compounds **12** (and, therefore, in silyl enol ethers **11**) relies on the assumption of suprafaciality in the sense of addition to diene **1b**.[4b]

(10) The cis/trans ratios in compounds **6** are for **6a** 12:1, for **6b** ~ 6:1, and **6c** 8:1.

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