forded **2j** in only 33% yield. Moreover, the hydrogen peroxide–sodium tungstate oxidation[16] of amines to oximes failed completely for **1j**. We feel that the ease of operation, availability of reagents, and acceptable yields will make our oxidative deamination sequence a synthetically useful process. The experimental procedures will follow in the microfilm edition; see paragraph at end of paper regarding supplementary material.

Supplementary Material Available. A detailed experimental section tabulating spectral data will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Business Office, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring code number JACS-75-6900.

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(13) In a typical ring opening experiment, 1 mmol of **5** was treated with 1 ml of 10 *M* KOH in H₂O, 20 mmol of acetone, and sufficient cosolvent (MeOH or DMF) to obtain 5 ml of total volume.
(14) Our failure to exclude completely the formation of the amide **6** in the ring opening of **5** led us to synthesize phenyl 2-pyridyl ketone and 2-pyridyl *tert*-butyl ketone. Not unexpectedly, the condensation of these ketones with amines **1** proceeded in low yield even under forcing conditions.
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Stephen E. Dinizo, David S. Watt*

Department of Chemistry, University of Colorado
Boulder, Colorado 80302
Received June 28, 1975

Nucleophilic Catalysis of the Aromatization of an Arene Oxide. The Reaction of Trimethylamine with 4-Carbo-*tert*-butoxybenzene Oxide

Sir:

The reactivity of arene oxides in solution is characterized by their facile isomerization to phenols (NIH-shift)[1] via specific acid and spontaneous pathways[2] as well as general acid catalysis.[3,4] The aromatization of substituted benzene oxides by either specific acid catalysis or spontaneous rearrangement exhibits a ρ^+ of ca. -7[5] and gives the corresponding phenolic products consistent with epoxide opening to the most stable carbonium ion.[6]

Benzene oxides are also subject to competing nucleophilic attack and are particularly susceptible to soft nucleophiles as evidenced by reports that benzene oxide itself reacts readily with azide and mercaptide anions, while is unreactive toward the hard nucleophiles NH_3 and $^-NH_2$.[7] To date, the competition between nucleophilic reactivity and spontaneous aromatization rates of arene oxides provides the most distinguishing feature between non-K-region oxides and the biologically important K-region oxides.[8] While trimethylamine is unreactive towards benzene oxide,[9] we have discovered via kinetic and isolation techniques the formation and subsequent aromatization of a 1,6-nucleophilic addition adduct of trimethylamine and 4-carbo-*tert*-butylbenzene oxide (**1**),[10] thus providing the first case of *nucleophilic catalysis* in the aromatization of an arene oxide.

The aromatization of (**1**) in water between pH 0 and 10 in the absence of buffer exhibited excellent *pseudo*-first-order kinetics (k_{obsd}). The pH-dependence of log k_{obsd} (Figure 1) follows the rate law of eq 1

$$k_{obsd} = k_H a_H + k_0 \tag{1}$$

where a_H is the hydrogen ion activity determined at the glass electrode, $k_H = 0.185 \ M^{-1} \ sec^{-1}$, and $k_0 = 1.55 \times 10^{-5} \ sec^{-1}$. The products were identified spectrophotometrically as a mixture of 94% *tert*-butyl *m*-hydroxybenzoate (**2**) and 6% *tert*-butyl *p*-hydroxybenzoate (**3**) by employing extinction coefficients and pK_a's of independently prepared samples of **2** (pK_a = 9.15 measured at 325 nm) and **3** (pK_a = 8.42 measured at 295 nm). The ratio of the two isomeric benzoates was constant over the pH-range studied. In contrast to previous studies on non-K-region oxides, a base catalyzed reaction predominated at high pH with the biphasic formation (280 nm) of a complex product mixture containing some *tert*-butyl *trans*-2,3-dihydroxy-2,3-dihydrobenzoate[12] between pH 10 and 14 (Figure 1).

The reaction of **1** with excess trimethylamine (TMA; 0.032–0.5 *M*; pK_a 9.95) at 30° (μ = 1.0, KCl) and constant pH (9.02–10.82) was found to be biphasic. Both the appearance (eq 2) and disappearance (eq 3) of intermediate (280 nm) were pseudo first order to greater than three half-lives.

$$k_{obsd_1} = k_1 [TMA]_T \frac{K_a}{(K_a + a_H)} \tag{2}$$

$$k_{obsd_2} = k_2 [TMA]_T \frac{K_a}{(K_a + a_H)} + \frac{k_3 K_w}{a_H} \tag{3}$$

The sole product of the reaction was identified spectrophotometrically as **2**. For the initial phase of reaction, plots of k_{obsd_1} vs. total TMA concentration ($[TMA]_T = [TMA] + [TMAH^+]$) at varying pH are linear giving coincident intercepts on the k_{obsd} axis near k_0 at $[TMA]_T = 0$. The slopes of these plots when plotted vs. $K_a/(K_a + a_H)$ were found to be linear of slope k_1 (Figure 2). For the second phase of the reaction, plots of k_{obsd_2} vs. $[TMA]_T$ at varying pH's were linear with pH-dependent intercepts on the k_{obsd}
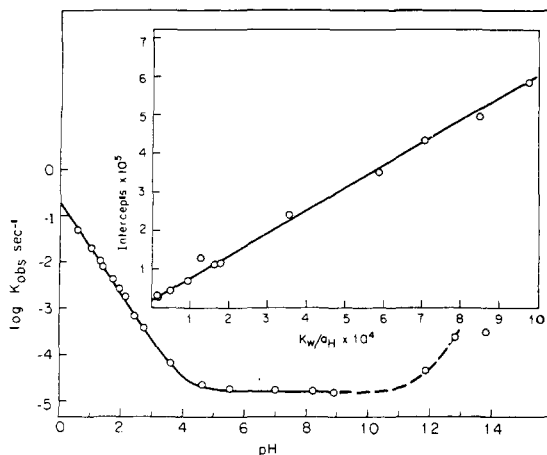
Figure 1. pH-rate profile for the rearrangement of **1** in water at 30° (μ = 1.0, KCl). The solid line was generated from eq 1. For the dashed portion, a hydroxide dependent rate term (k_{HO}-[HO$^-$] where k_{HO^-} = 2.5 × 10^{-3} M^{-1} sec^{-1}) was added to eq 1. Insert to figure: Plot of the intercepts derived from K_{obsd_2} vs. [TMA]$_T$ plots against hydroxide ion concentration.
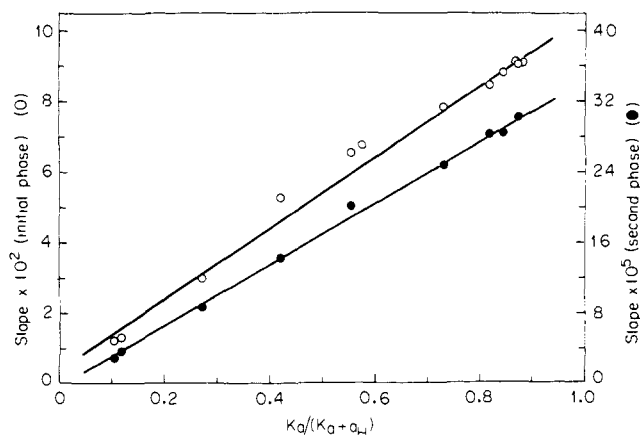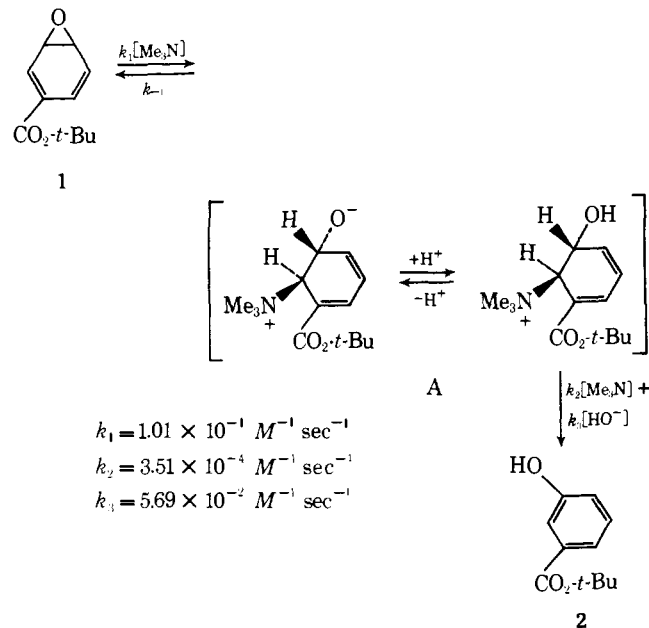

Figure 2. The slopes derived from plots of k_{obsd_1} (O) or k_{obsd_2} (●) vs. [TMA]$_T$ plotted against the fraction of TMA as the free amine.

Scheme I

$k_1 = 1.01 \times 10^{-1}$ M^{-1} sec^{-1}

$k_2 = 3.51 \times 10^{-4}$ M^{-1} sec^{-1}

$k_3 = 5.69 \times 10^{-2}$ M^{-1} sec^{-1}

axis at [TMA]$_T$ = 0. The value of k_2 was obtained as the slope of a plot of the slopes of the buffer dilution plot vs. $K_a/(K_a + a_H)$ (Figure 2) and the value of k_3 was obtained by plotting the intercepts of the buffer dilution plot vs. K_w/a_H (insert to Figure 1). The kinetic results are readily interpreted in terms of Scheme I where nucleophilic attack of trimethylamine at the 3-position of **1** results in the formation of intermediate A[13] which then decomposes to the phenol via general base catalyzed (hydroxide and amine) elimination. In the pH-range employed all A exists in the undissociated form and the rate constant k_{-1} is too small to be detected.

Under carefully controlled conditions the chloride salt of A could be obtained from a reaction solution by evaporation and isolated as a solid mixture with trimethylamine hydrochloride. Both the uv spectra and kinetics of decomposition at 280 nm for this solid were identical with that for A described above. The 270-MHz ^{1}H NMR spectrum (CDCl$_3$) of this solid is in agreement with structure A shown in Scheme I and gives rise to the values shown below. The singlet at δ 4.69 is assigned to the proton on the carbon bearing the trimethylammonium group (H$_6$) and is inconsistent with other positional isomers of A since observable coupling with an adjacent vinyl proton would be expected.

A
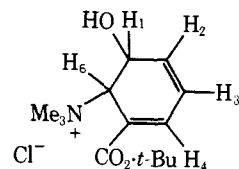
	δ	J (Hz)
H$_1$	5.13	$J_{1,3} = 6$
H$_2$	6.84	$J_{2,3} = 10; J_{2,4} = 3.8$
H$_3$	6.40	
H$_4$	7.54	
H$_6$	4.69	
-NMe$_3^+$	3.29	
-CO$_2$-t-Bu	1.49	

Primary amines also react with **1** to give apparent nucleophilic intermediates whose breakdown to products are, as expected, more complex than in the case of A. The high nucleophilicity of trimethylamine toward arene oxides,[8] coupled with its leaving ability and basicity account for its catalytic effect on the aromatization of **1**. It has recently been shown that K-region oxides have an enhanced susceptibility towards nucleophilic attack compared to non-K-region oxides,[8] thus nucleophilic catalysis may also be found for this important class of compounds.

Nucleophilic catalysis of arene oxide aromatization provides an alternate route to the NIH-shift. Evidence has recently been presented by Tomasziewski, Jerina, and Daly[14] that an alternate to the NIH-shift is prevalent in the hydroxylation reaction of benzenoid compounds by hepatic monooxygenases. Further, the monooxygenase reaction is characterized by a C-H(D) isotope effect which could derive from the elimination step (Scheme I) of nucleophilic catalysis.

Since **1** exhibits a slower spontaneous aromatization rate than benzene oxide,[2] one might expect nucleophilic attack by hard nucleophiles to compete more favorably with aromatization in this system, as observed; however, we have also detected nucleophilic reactivity of amines with 4-carboxybenzene oxide anion whose spontaneous aromatization rate is tenfold greater than that for benzene oxide. It is ap-

parent, then, that substituent effects governing these competitive pathways are complex and studies are underway to further probe the nature of these effects.

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(9) No nucleophilic reaction between benzene oxide and 1 *M* trimethylamine at pH 9.90 was observed.
(10) The oxide 1 actually exists in equilibrium with its oxepin valence isomer. For 1 the equilibrium favors the oxepin isomer in solution.[11]
(11) R. M. DeMarinis, C. N. Filer, S. M. Waraszkiewicz, and G. A. Berchtold, *J. Am. Chem. Soc.*, **96**, 1193 (1974).
(12) It has previously been reported that 1 provides *tert*-butyl *trans*-2,3-dihydroxy-2,3-dihydrobenzoate when treated with LiOH in aqueous dioxane.[11] Our results indicate that the optimum pH for the formation of this diol in aqueous solution is ca. pH 12-13.
(13) 1,6-Nucleophilic addition of HO⁻ and MeO⁻ to 1 has been observed previously.[11] The stereochemistry of addition was established as trans, and is assumed here for A by analogy.
(14) J. E. Tomasziewski, D. M. Jerina, and J. W. Daly, *Biochemistry*, **14**, 2024 (1975).
(15) National Institutes of Health Postdoctoral Fellow, 1974–present.

**David M. Johnson,[15] T. C. Bruice***

*Department of Chemistry, University of California
Santa Barbara, California 93106*

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Reactions on Coordinated Molecules. IV. The Preparation of Tris(cis-diacetyltetracarbonylmanganate)aluminum. A Metalloacetylacetonate Complex

Sir:

We wish to report the preparation of a complex which we believe is the first number of an extensive class of coordination compounds. When nucleophilic attack on an acyl complex is directed to a carbonyl ligand which is cis to the acyl ligand, the acyl–metalate anion, **1**, produced is electronically equivalent to the acetylacetonate anion.

1
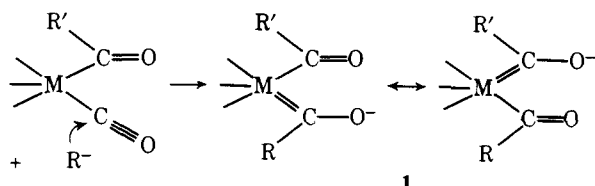
where M is a transition metal atom.

Anion **1** is similar to the acetylacetonate anion in that the methine group is replaced by the organometallic complex. We report now the preparation of the first example of a "metallo-acac" anion and the complexation of this anion to
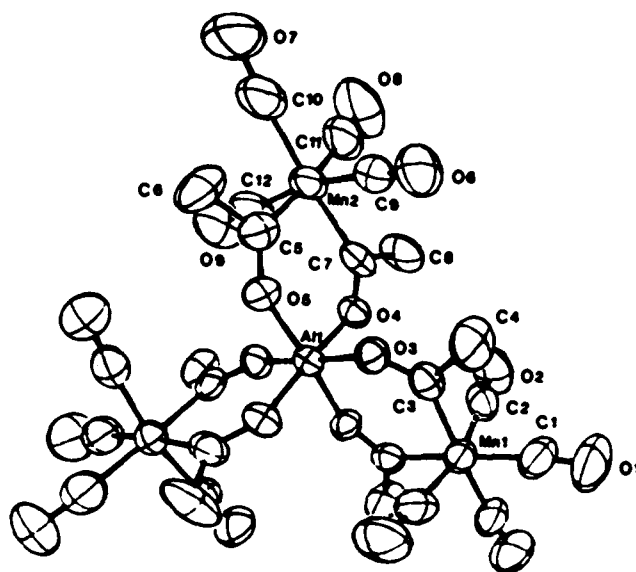

Figure 1. A view of the molecular structure of one of the independent molecules of Al[Mn(CO)₄(COCH₃)₂]₃ showing the atomic numbering scheme. The sizes and shapes of the atoms are determined by their final thermal parameters and by their perspective view.

an aluminum(III) cation forming a neutral tris-chelate complex.

To a solution of 1.0 g (4.2 mmol) of acetylpentacarbonylmanganese in 15 ml of ether was added 3.0 ml of 1.56 *M* methyllithium solution (4.7 mmol, in ether) at 0° over a 45-min period. During this addition the reaction solution became deep yellow and an infrared spectrum of this solution indicated that the terminal carbon monoxide ligand stretching frequencies of the reactant complex had shifted 70 cm⁻¹ to lower frequency, and that the acyl band at 1650 cm⁻¹ in the acetyl complex disappeared concomitantly with the appearance of a similar band at 1585 cm⁻¹. These data reflect the formation of the bis(diacetyl)metalate anion, **2**.[1]
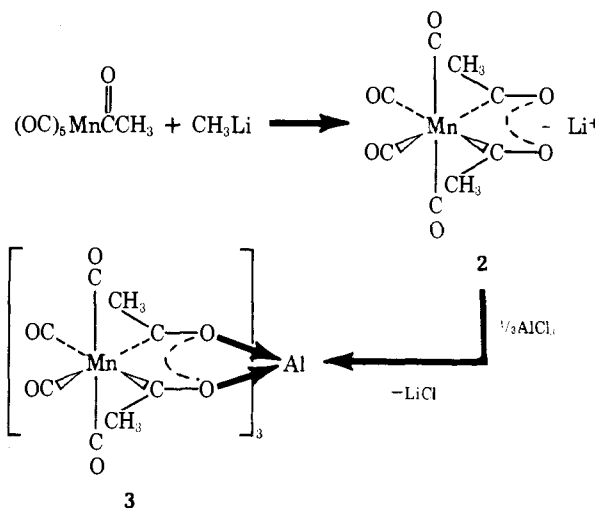
To this solution is added 0.19 g (1.4 mmol) of anhydrous aluminum chloride in 5 ml of ether over a 5-min period. The reaction solution is stirred for 1.5 hr during which time a light colored solid precipitated. The solution is filtered and the solid is washed with 2 × 4 ml of ether and dried at reduced pressure affording 0.88 g of an off-white powder. This solid is extracted into 30 ml of toluene at room temperature and filtered affording 0.15 g (82%) of a white solid identified as lithium chloride. The yellow filtrate is cooled slowly to −78° affording 0.42 g (38%) of the title compound, **3**, as pale yellow hexagonal needles: mp darkens at