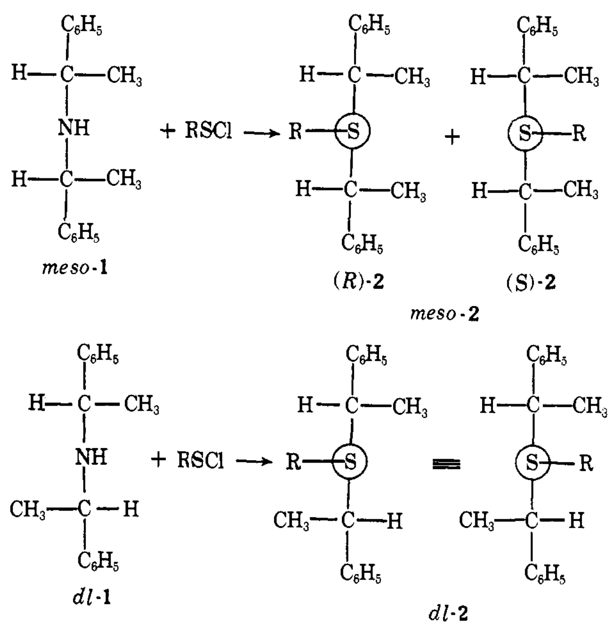
activation at the coalescence point, which can be accurately determined using approximate equations or calibration curves,[13] were comparable in the two compounds. The barrier in *dl*-**2** was found to be intermediate between the free energies of activation for the forward and reverse interconversions of the two diastereomers of *meso*-**2**: *dl*-**2**, $\Delta\nu = 5.6$ Hz, $T_c = 91°$, $\Delta G^{\ddagger} = 19.6$ kcal/mol; *meso*-**2**, $\Delta\nu = 4.6$ Hz, $T_c = 86°$, $\Delta G^{\ddagger}$(forward) = 19.5 kcal/mol, $\Delta G^{\ddagger}$(reverse) = 20.5 kcal/mol.

The presence of pseudoasymmetry in *meso*-**2** provides a convenient and unequivocal means for the assignment of configuration to *meso*-**1**. Such a method complements that of Hill and Chan[14] which permits unequivocal assignment of configuration to the *dl* isomer. In the present instance, the *N*-benzyl derivative of *dl*-**1** (prepared by reduction of the benzamide) features an AB quartet for the *N*-benzylmethylene protons: $\Delta\nu_{AB} = 0.45$ ppm, $J_{AB} = 15$ Hz. The present method offers a useful alternative or supplement to the method of Hill and Chan when both isomers are not available or in instances when the latter method is not successful.[15]


meso-**1**
(*R*)-**2**
(*S*)-**2**
meso-**2**
dl-**1**
dl-**2**

R = 2,4-dinitrophenyl

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(13) D. Kost, E. H. Carlson, and M. Raban, *Chem. Commun.*, 656 (1971).

(14) R. K. Hill and T.-H. Chan, *Tetrahedron*, **21**, 2015 (1965).

(15) We thank the National Science Foundation for support of this work.

Daniel Kost, Morton Raban*
Department of Chemistry, Wayne State University
Detroit, Michigan 48202
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Primary Amine Catalysis of the Cleavage of Mesityl Oxide to Acetone

Sir:

In the course of a previous investigation[1] of primary amine catalysis of the dealdolization of diacetone alcohol, we found that mesityl oxide (an impurity in commercial diacetone alcohol) reacts rapidly in moderately basic solution with *n*-propylamine. Although this reaction had previously been observed[2] with ethylamine, neither characterization of the product nor investigation of the reaction mechanism was attempted. We now wish to report that this reaction is the primary amine catalysis of the cleavage of mesityl oxide to acetone, and furthermore, that the mechanism does *not* involve the intermediate formation of diacetone alcohol.

On adding mesityl oxide to a solution of *n*-propylamine in water, a biphasic reaction may be observed,[3] consisting of an initial, rapid first-order decay of mesityl oxide, followed by a slower first-order decay until no detectable mesityl oxide is left. The rate constants for both reactions increase with increasing concentration of amine. In addition, the pseudoequilibrium reached at the end of the first decay is proportional to the concentration of the amine. It is important to note that the kinetics require one molecule of amine as a reactant for the first step and a second molecule of amine as a catalyst for the second step. This type of kinetic behavior may be analyzed in terms of eq 1. Values of the

$$\text{mesityl oxide} + \text{amine} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{intermediate} \xrightarrow{k_2[\text{amine}]} \text{acetone} + \text{amine} \quad (1)$$

pseudoequilibrium constant K (= [intermediate]/[mesityl oxide][amine]) calculated from initial and infinity absorbances for the first decay were found to vary little over a wide pH range (Table I). The fact that these values are essentially invariant over a pH range of more than 1 pH unit on each side of the pK_a of *n*-propylamine (pK_a = 10.9)[1] indicates that not only does the intermediate have the elements of the amine in it but that it has a pK_a very similar to *n*-propylamine itself.

Table I. Variation with pH of Observed Equilibrium Constants for Formation of the Michael Adduct from Mesityl Oxide and *n*-Propylamine[a]

pH	*K*
9.59	11.4 ± 1.5
10.00	11.4 ± 1.0
10.42	15.4 ± 0.3
10.80	19.0 ± 1.1
11.36	19.4 ± 2.8
11.76	21.2 ± 2.6
12.42	23.1 ± 2.0

[a] Equilibrium constants were calculated using the *total* amine concentration.

The intermediate was identified as the Michael adduct of *n*-propylamine and mesityl oxide by a consideration of the following changes in the nmr spectrum as the reaction proceeds. Mesityl oxide shows a spectrum consisting of four singlets at δ 6.1 (1 H), 2.1 (3 H), 2.0

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(1) R. M. Pollack and S. Ritterstein, *J. Amer. Chem. Soc.*, in press.

(2) R. W. Hay and K. R. Tate, *Aust. J. Chem.*, **19**, 1651 (1966).

(3) The reaction was monitored spectrophotometrically by following the loss of mesityl oxide at 243 nm. The concentration of mesityl oxide was approximately 2×10^{-4} *M*. The pH was maintained by using *n*-propylamine and its hydrochloride as a buffer at the lower pH values and by addition of KOH at higher pH. The temperature was kept at 25.0 ± 0.2° and potassium chloride was added where necessary to maintain an ionic strength of 0.2.

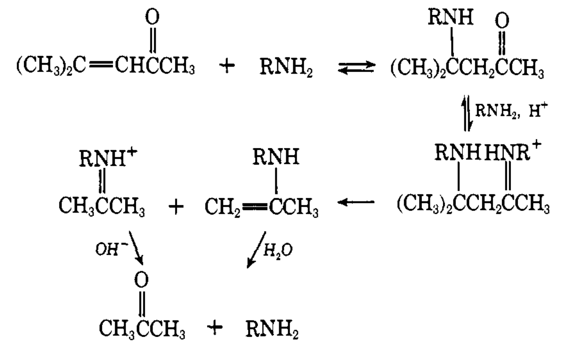
(3 H), and 1.9 (3 H). On addition of mesityl oxide to an aqueous solution of *n*-propylamine, the three signals at highest field are easily observable. The two at δ 2.1 and 2.0 disappear with concurrent appearance of a new signal at δ 1.1. The new signal may be attributed to the *gem*-dimethyl groups of the intermediate Michael adduct. The methyl group α to the carbonyl is expected to absorb about the same place as one of the methyls of mesityl oxide, which accounts for the lack of disappearance of one of the three peaks. Furthermore, if the spectrum is taken in D_2O, all three of the high-field peaks of mesityl oxide disappear since the methyl peak of the intermediate α to the carbonyl is free to exchange with D_2O. The vinyl peak of mesityl oxide also disappears showing that the intermediate is saturated. The multiplet due to the methylene group α to the amine group of *n*-propylamine (δ 2.5) broadens appreciably indicating that there is a change of chemical environment of these protons as well. The time scale of these changes is that expected from the kinetics. At much longer times, the nmr spectrum becomes identical with that of an authentic mixture of acetone and *n*-propylamine (δ 2.1).

Rate constants for the formation of intermediate (k_1) and the breakdown of intermediate (k_2) were obtained by a modification of the technique described by Fersht and Jencks.[4] These rate constants are based on total amine concentration. A plot of log *k vs.* pH is given in Figure 1.

The addition reaction depends on a single group of pK_a 10.9, which may be identified as the amine. This result can be accommodated by a slow attack of the nucleophile on unprotonated carbonyl compound. It is also possible that addition proceeds through slow formation of a Schiff base followed by a rapid attack of amine. We are currently investigating this possibility.

The breakdown of the intermediate depends on two groups with pK_a values of 10.8 and 10.9. In the transition state, one of these groups must be protonated and the other free. A reasonable mechanism is given in Scheme I.

Scheme I



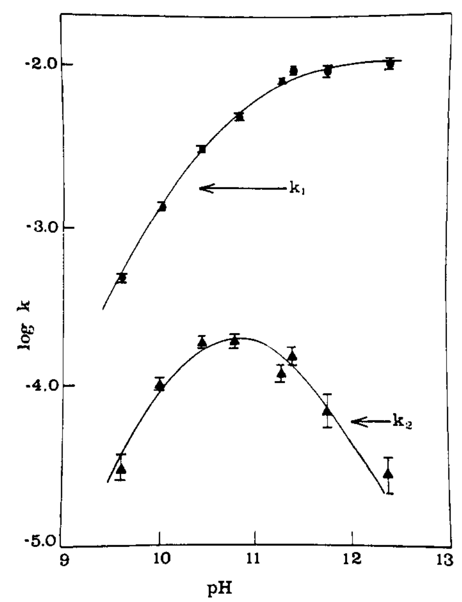


Figure 1. Variation of second-order rate constants (M^{-1} sec^{-1}) with pH for reaction of mesityl oxide with *n*-propylamine (H_2O, μ = 0.2, 25.0°).

The requirement for a single proton in the transition state is in sharp contrast to the analogous cleavage of the Schiff base of diacetone alcohol,[1] which involves breakdown through a neutral transition state. This difference is presumably due to the much greater basicity of the amine than the alcohol. This mechanism for the interconversion of mesityl oxide and acetone bypassing the formation of diacetone alcohol finds support in the report of Yasnikov[5] that amine catalysis of the self-condensation of butyraldehyde occurs in part without the intermediate formation of the aldol product. Additional evidence that diacetone alcohol is not an intermediate is found in the fact that the rate of *n*-propylamine-catalyzed cleavage of diacetone alcohol is too slow to account for the observed cleavage of mesityl oxide in the pH range 9.5–10.5.

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(5) T. S. Boiko, N. V. Volkova, and A. A. Yasnikov, *Ukr. Kim. Zh.*, **29**, 1179 (1963).

Ralph M. Pollack,* David Strohbeen
Department of Chemistry
University of Maryland Baltimore County
Baltimore, Maryland 21228

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Delayed Fourier Transform Proton Magnetic Resonance Spectroscopy

Sir:

We describe here a simple modification of standard Fourier transform (FT) nmr methods[1] which may be used in analyzing spectra which contain both broad and narrow components. Frequently, line width and intensity measurements on the narrower resonances of such spectra are difficult, because these peaks appear superimposed against the broader resonances. It is possible, however, to filter out the broad resonances from the spectrum by introducing a delay time between the end of the rf pulse and the start of data collection. Each component of the transient signal will then have decayed to exp($-\Delta\tau/T_2$) of its initial value by the time

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