

TABLE IV
RATE DATA FOR OXIDATION OF VI AND VII
WITH ACETYL PEROXIDE IN ACETONITRILE AT 30°

Amine	Initial concentrations		$k' \times 10^4 \text{ sec}^{-1}$	Standard deviation
	[Peroxide] $\times 10^{-2}$	[Amine] $\times 10^{-4}$		
VI	2.48	1.57	0.220	0.008
	2.48	1.57	0.217	0.012
	2.48	1.57	0.218	0.012
VII	2.48	1.52	0.208	0.014
	2.48	1.52	0.214	0.017
	2.48	1.52	0.209	0.016

VIII probably does not involve breaking of the nitrogen-hydrogen bond in the transition state of the reaction and may likely be an electron-transfer process.

Experimental Section

Materials.—*tert*-Butyl peroxide (Wallace and Tiernan, Inc.) and a 25% solution of acetyl peroxide in dimethyl phthalate (Wallace and Tiernan, Inc.) were used without further purification. *tert*-Butyl peracetate (Wallace and Tiernan, Inc.) (75% perester in benzene) was purified by vacuum distillation. The following commercial reagents were distilled twice before using: 2-butanol (from sodium), tetrahydrofuran (from sodium), and acetonitrile (from phosphorous pentoxide).

3,5-Dicarbethoxy-1,4-dihydro-2,6-lutidine (VI) was prepared from acetoacetic ester, formaldehyde, and ammonia by the method of Singer and McElvain⁹ (mp 183–185°).

1-Deuterio-3,5-dicarbethoxy-1,4-dihydro-2,6-lutidine (VII) was prepared by allowing a mixture of 5 g of VI to reflux for 2 hr with 10 ml of deuterium oxide in 100 ml of dimethoxyethane. The compound was isolated and recrystallized from ethanol and the process repeated twice with fresh deuterium oxide. After the final exchange, no nitrogen-hydrogen bond could be observed in either the infrared or the nmr spectra of the material.

***O*-*d*-2-Butanol (V)** was prepared by reaction of the sodium alkoxide with deuterium oxide in the following manner. Freshly distilled 2-butanol (500 ml) and sodium (20 g) cut in small pieces

(9) A. Singer and S. M. McElvain, "Organic Syntheses," Coll. Vol. II, Wiley, New York, N. Y., 1943, p 214.

were placed in a 1-l. round-bottomed flask equipped with a reflux condenser. After the initial rapid reaction the mixture was heated at reflux for an additional 16 hr during which period all of the sodium reacted. Excess 2-butanol was removed under a vacuum leaving a white solid which was heated under vacuum for an additional 24 hr. Deuterium oxide (20 ml) was added to the dry solid producing a reddish brown mixture. The organic layer was distilled twice yielding *O*-*d*-2-butanol that by nmr analysis was 99% deuterated (30.2 g, 47% theory).

Peroxide Decomposition Rates.—The rates of reaction of *tert*-butyl peroxide in 2-butanol and *O*-*d*-2-butanol were determined by the gas chromatographic method described previously.³ The decomposition rate of *tert*-butyl peroxide in the tetrahydrofuran solutions of VI and VII were also made by the gas chromatographic analysis of the unreacted peroxide as previously described.⁴

The decomposition rates of acetyl peroxide and *tert*-butyl peracetate in the presence of 2-butanol and *O*-*d*-2-butanol were determined by the method described by Silbert and Swern;¹⁰ 1-ml samples of the reaction mixture were pipetted into a flask through which nitrogen had been passed for 20 sec. A saturated sodium iodide solution (about 2 ml) and 15 ml of freshly distilled glacial acetic acid containing 0.002% ferric chloride were added to the contents in the flask. The flask was stoppered and permitted to stand in the dark for 10–15 min. About 50 ml of distilled water was added to the solution which was titrated to a starch-iodine end point with 0.2 *N* thiosulfate to determine the amount of molecular iodine produced. A blank determination was run on all of the reagents.

Spectrophotometric Determination of Oxidation of Dihydro-lutidines with Acetyl Peroxide.—Stock solutions of VI and VII in acetonitrile and of the acetyl peroxide-dimethyl phthalate solution in the same solvent were prepared. Samples of these solutions were thermostated at 30° before mixing. Immediately after mixing, the solutions were placed in a thermostatically controlled cell compartment of a Beckman DU spectrophotometer. The rates of reaction of the dihydropyridine derivatives were followed by measuring their absorption at 363 m μ as a function of time.

Registry No.—I, 110-05-4; II, 110-22-5; III, 107-71-1; 2-butanol, 78-92-2; V, 4712-39-4; VI, 1149-23-1; VII, 25894-44-4.

(10) L. S. Silbert and D. Swern, *Anal. Chem.*, **30**, 385 (1958).

Substituent Effects in Alkali Metal-Ketyl Ion Pairs. An Infrared Scrutiny

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The carbonyl stretching frequency (ν) of alkali metal-4,4'-disubstituted ketyl ion pairs shows a startling deviation from the expected influence of five para substituents. Measurements indicate that the ketyl C=O bond is strengthened, rather than loosened, by electron-donating substituents. Plots of σ_{R}^+ vs. ketyl frequency are given. A possible explanation lies in the consideration of ion pairing by the counterion M^+ with increased electron density at the ketyl site. Such ion pairing might be able to reduce the antibonding influence of the added electron, thus allowing bonding π electrons to exert a stronger bonding force between the carbon and the oxygen atoms.

The utility of the carbon-oxygen stretching frequency of ketones as a sensitive indicator of electron density changes has long been recognized. Shifts in the carbonyl frequency are subject to both inductive and mesomeric effects which change the electron density at the carbon-oxygen bond.² Correlation of Hammett σ values with the carbonyl stretching frequencies in

five 4,4'-disubstituted benzophenones has been shown to be nearly linear.³ In essence, the studies all show that the greater the electron density at the C=O site, the lower the frequency (in cm^{-1}).

A one-electron reduction of a ketone results in a ketyl with the commonly given valence bond structure of $>\text{C}-\bar{\text{O}}$. Such a structure does not reflect the fact that only one of the π electrons of the C=O bond has been essentially "cancelled" by the introduction of the new electron into the lowest antibonding orbital of the

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(2) (a) R. E. Kagarise, *J. Amer. Chem. Soc.*, **77**, 1377 (1955); (b) N. B. Colthup, L. H. Daly, and S. E. Wiberley, "Introduction to Infrared and Raman Spectroscopy," Academic Press, New York, N. Y., 1964, p 241 ff.

(3) N. Fuson, M.-L. Jósien, and E. M. Shelton, *J. Amer. Chem. Soc.*, **76**, 2526 (1954).