type basis sets. A detailed report on the crystallographic and molecular orbital studies is in preparation.

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Nucleophilic Substitution at the Alkoxyl Carbon of Imidates[1]

Sir:

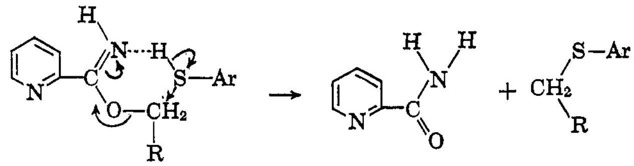
It is well known that, generally speaking, substitution in derivatives of carboxylic acids, such as esters and imidates, tends to occur at the central sp^2 carbon rather than at the sp^3 carbon of the alkoxyl group. Exceptions to this trend are the thermal decomposition of imidate hydrochlorides (Pinner cleavage),[2] the alkyl-oxygen fission of esters of tertiary alcohols,[3] and the nucleophilic substitution reactions of esters in which a highly electron-withdrawing substituent (*i.e.*, N-phthalimido)[4] is present at the α-carbon of the alkoxyl group.

In search of a selective method for the replacement of a hydroxyl in polyfunctional alcohols by a suitable nucleophile, the polyfunctional alcohol was first converted to the monoimidate by reaction with 2-cyanopyridine under base-catalyzed conditions,[5] and the resulting imidate was then treated at *ca.* 150° with arylthiols to give the products of the desired nucleophilic substitution reaction at the sp^3 carbon of the alkoxyl group, namely, hydroxyalkyl aryl sulfides, and the novel "leaving group," namely, 2-pyridinecarboxamide.

Thus, the monoimidate of ethylene glycol, upon treatment with *o*- or *p*-thiocresol, *p*-*t*-butylthiophenol, and *p*-bromothiophenol, gave the corresponding 2-hydroxyethyl aryl sulfides in yields as high as 64% of theoretical. The products gave the correct microanalytical results and infrared spectra identical with those of authentic samples prepared by the reaction of the thiols with ethylene chlorohydrin.[6]

The reaction can be carried out in excess of the thiol, or by using diethylbenzene or dimethylformamide as solvent. The yields of the reaction improved when nonpolar solvents were employed, and this observation, as well as the failure of the desired nucleophilic substitution when the hydrochloride or picrate of the imidate was treated with sodium thiocyanate, potassium iodide, or sodium mercaptides, suggest that the reaction occurs in the complex of the imidate and the conjugated acid of the nucleophile by an intramolecular mechanism.

In accord with the postulated mechanism is the observation that the reactions of benzylamine, piperidine,



Ar = *o*- or *p*-$CH_3C_6H_4$, *p*-*t*-BuC_6H_4, *p*-BrC_6H_4; R = $HOCH_2$

and morpholine with the imidate derived from 2-cyanopyridine and ethylene glycol produce the conventional attack at the sp^2 carbon. This course of the substitution reaction was proven by the isolation of the N-benzylamide and the N-piperidino- or N-morpholinoamidines (the latter in the form of the picrates), respectively, derived from 2-pyridinecarboxylic acid. Also, the recent report[7] of the formation of thiono esters by the base-catalyzed reaction of imidates with hydrogen sulfide indicates that strong bases, or anionic nucleophiles, react preferentially at the sp^2 carbon, while nucleophiles capable of hydrogen bonding with the imidate favor the intramolecular reaction path leading to the SN reaction at the sp^3 carbon of the alkoxyl group.

The novel substitution reaction is being extended to more complex polyfunctional alcohols and to nucleophiles other than thiols. Also, the optimum conditions for the reaction are being determined.

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Physical Theory of Chemiluminescence in Systems Evolving Molecular Oxygen[1]

Sir:

Chemiluminescence of organic molecules is a frequently observed phenomenon in liquid reaction systems and most often accompanies oxidation in the presence of hydrogen peroxide or molecular oxygen. An inorganic chemiluminescent reaction system which has been extensively investigated recently[2,3] involves the reaction in alkaline solution of H_2O_2 with either Cl_2 gas or OCl^- (hypochlorite ion). It is now generally agreed that the observed red (and infrared) chemiluminescence in this inorganic case arises from metastable excited states of molecular oxygen produced in the reaction. These observations and interpretations extend the much earlier ones made by Groh and Kirrmann.[4] New observations made in this laboratory now permit the projection of a general theory of chemiluminescence which unites these two classes of phenomena, *i.e.*, organic molecule chemiluminescence in oxidation reactions in solution and excitation of metastable states of molecular oxygen in peroxide systems.

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