alcohols (we observe a half-life of ca. 4 hr for **1**, R = Ph, in methanol at room temperature) also provide an attractive basis for further investigation.

Our preliminary results confirm the impression[2,15] that type **1** compounds can take part in a great variety of reactions, including free-radical processes, nucleophilic displacements and oxidation-reduction phenomena.

Thus, 0.1 *M* methanolic solutions of **1** react instantaneously (cf. ref 15b) with methanolate solution, the corresponding methyl esters being formed quantitatively. From competitive reactions involving **1**, R = *m*-chlorophenyl, and **1**, R = Ph, and using small proportions of CH_3ONa in methanol, it is found that the relative rate (m-Cl/H) ≈ 2.0 at 20°. The reaction with methanol-pyridine takes several minutes to reach completion and is also more selective. Finally, the high reactivity with 0.2 *M* methanolic thioanisole (50% conversion of **1**, R = Ph in ca. 2 min) is noteworthy by comparison with sulfides in reaction with other peroxy compounds, such as acylperoxides,[16] which are formally analogs of **1**. This is in line with expectations in considering the relative leaving group facility of NO_3^- and RCO_2^- in nucleophilic displacements.

Our investigations as regards preparation and properties of **1** are being continued.

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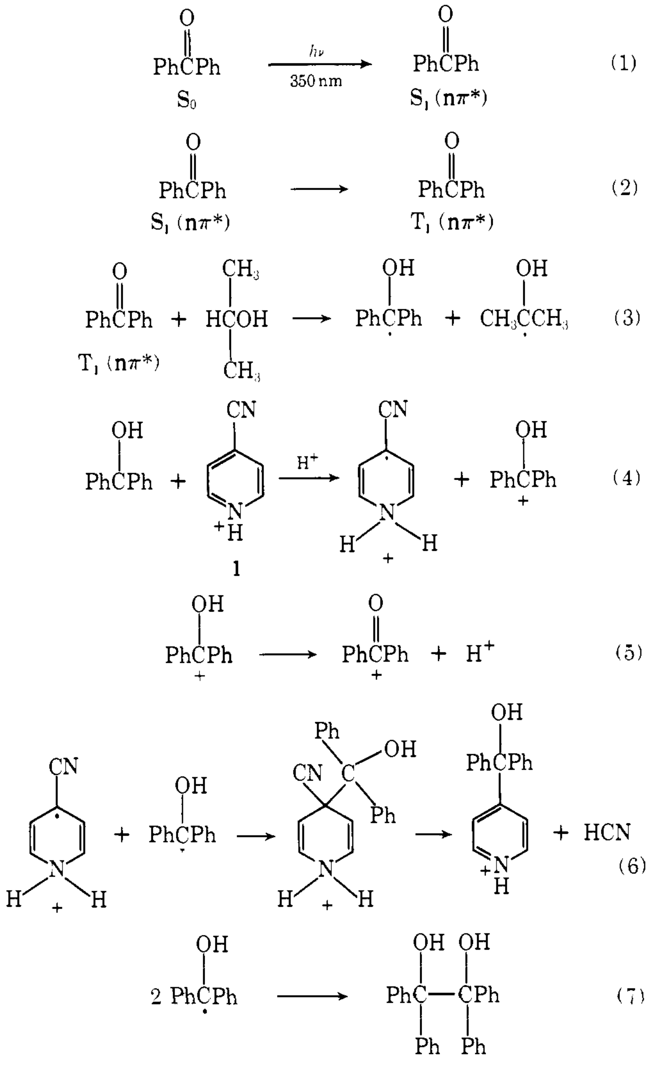
The Photoinitiated Electron Transfer–Substitution Reaction of Diphenyl Ketyl with Protonated 4-Cyanopyridine

Sir:

Recent findings have demonstrated that substituent effects can dramatically alter the course of homolytic substitution reactions of protonated heteroaromatic bases. For example, reactions of radicals with pyridines containing electron withdrawing substituents in the 4 position, in acid solution, form products of addition to the 2 position in better yield and with higher selectivity than is found with pyridine itself under the same conditions.[1] This high sensitivity to substituent effects has been explained in terms of a transition state similar to a charge-transfer complex in which a positive charge develops on the attacking radical.[2] Nucleophilic π type radicals, such as benzyl, in which the incipient positive charge can best be stabilized do, in fact, produce the highest yields of substitution products.

Scheme I

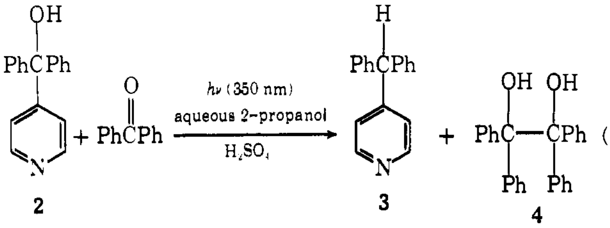


We would now like to report a novel S_R reaction of protonated 4-cyanopyridine (**1**) in which substitution occurs in the 4 position, resulting in the displacement of the cyano group. This reaction is best explained (Scheme I) by an electron transfer from the π type diphenyl ketyl radical to the 4-cyanopyridinium ion in 1 *M* sulfuric acid in aqueous 2-propyl alcohol (1:3). The donor radical is conveniently produced photochemically by the well-known process of hydrogen atom abstraction by the T (nπ*) state of benzophenone.[3,4] The reaction mixtures were degassed by four successive freeze-vacuum-thaw cycles and the irradiations were carried out under nitrogen in a Model RPR-100 Rayonet photochemical reactor at 350 nm using quartz reaction vessels.[5,6] Three of the major products formed in the reaction are diphenyl(4-pyridyl)carbinol (**2**), mp 235.5-236.5 (7.2% yield) (lit.[7] 235°), 4-benzhydrylpyridine (**3**), mp 123-124° (18.7% yield) (lit.[7] 125°), and benzopinacol (**4**).[8] Another product for which no structure has yet been assigned has a molecular weight of 348 by mass spectroscopy and melted at 146.5-147° (2% yield). This compound contains cyano, isopropyl, and benzhydrol groups and is apparently the result of two radical substitution reactions of the same pyridine ring.

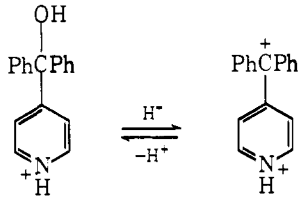
Five additional basic compounds (approximately 60% yield) were isolated from the reaction mixture in semipure form and are presently under investigation. These are highly polar substances which contain neither cyano nor benzhydryl groups. Pyridine or unreacted 4-cyanopyridine could not be detected among the reaction products.

Though dimethyl ketyl can also transfer electrons to suitable acceptors very efficiently,[9] in this reaction, concentration factors should favor diphenyl ketyl as the transfer agent.[10]

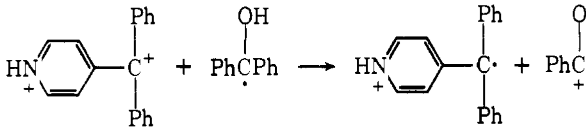
4-Benzhydrylpyridine (**3**) is not a primary product of reaction but has been shown to form in 71% yield when **2** is irradiated in acidic aqueous 2-propanol under the same conditions as described for **1** (eq 8). In acid solution, if an equilibrium is established between protonated **2** and carbonium ion **5** (eq 9), then an electron would most likely transfer directly to the carbonium ion center of **5** (eq 10) forming the radical **6** which would subsequently form **3** by hydrogen atom abstraction. Even if the equilibrium in eq 9 is unfavorable, the formation of the more stable radical **6** would be rapid since the electron exchange (eq 10) should occur at a diffusion controlled rate.[11]



2 3 4 (8)

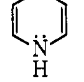


2 5 (9)



5 6 (10)

Preliminary results indicate, furthermore, that the electron transfer step is very sensitive to both the electron donor capacity of the substituent on the pyridine ring as well as the steric hindrance about the ketyl donor radical. This is demonstrated by the facts that 4-methoxypyridinium ion does not react with diphenyl ketyl, presumably because of the considerable ground state contribution from structure **7**,[1,12] and duryl phenyl ketyl[13] does not react with 4-cyanopyridinium ion.



7

Pyridinyl radicals are known to dimerize or disproportionate by second-order kinetics.[9] Though there is some infrared evidence for the presence of 4,4′-dipyridyl among the reaction products, under the conditions used, dimerization does not appear to be a major pathway.

We are presently studying these reactions by ESR and investigating the reaction of diphenyl ketyl with other substituted pyridinium ions and other molecules, and these will be subjects of subsequent reports.

Acknowledgment. We would like to thank Professor Philip Rieger and Dr. Nancy Rieger, Department of Chemistry, Brown University, for the determination of the ESR spectra used in this study and the Reilly Tar and Chemical Corporation for generous samples of substituted pyridines.

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Effects of Molecular Complexing on the Properties of Binary Nematic Liquid Crystal Mixtures

Sir:

In order to achieve extended liquid crystalline temperature ranges, binary systems offer the advantage of frequently exhibiting eutectic behavior in their solid → mesophase transition while the mesophase → isotropic transition temperature varies linearly with composition. In particular, several binary nematic systems have been studied,[1-7] and only small deviations from linearity in the nematic → isotropic transition temperatures (T_{NI}) are noted when there are significant differences in molar volumes or densities of the components. This general behavior has been satisfactorily accounted for theoretically by Humphries and Luckhurst.[8]

It seemed to us that large deviations in T_{NI} as well as the solid → nematic transition temperature (T_{SN}) should be possible if molecular complex formation took place between the components of the binary system. Further, as opposed to the usual deviations in T_{NI} being depressions of the melting point,[9] in the case of complex formation, *increases* in the