the exchange may be between pyridine and solvent or between pyridines on different molecules *via* an intermolecular process. It is obvious that in view of the dramatic temperature (and solvent) effect on ligand lability, as reflected in the coupling constant, caution must be exercised in drawing conclusions from nmr data and other solution properties of olefin complexes. Further work is in progress.

Syntheses. The ethylene–pyridine complexes were prepared by the reaction of the appropriate pyridine with an aqueous solution of Zeise's salt, $K(C_2H_4PtCl_3)$. The *cis*-2-butene- and *trans*-2-butene–pyridine complexes were prepared by dissolving the corresponding ethylene–pyridine complex in chloroform, cooling to 0°, and adding liquid olefin to the flask. The flask was gradually brought to room temperature with vigorous magnetic stirring. Repetition of the process was necessary for quantitative displacement of the ethylene. All compounds were recrystallized from chloroform–pentane.

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The Photochemical Decomposition of Triphenylboron and Some of Its Complexes

Sir:

In earlier work[1,2] we have described the intramolecular conversion of sodium tetraphenylborate by light to a mixture of hydrocarbons, consisting of biphenyl, 1-phenyl-1,4-cyclohexadiene, 3-phenyl-1,4-cyclohexadiene, and 1-phenyl-1,3-cyclohexadiene as well as *m*- and *p*-terphenyls. The ratio of the amounts of biphenyl and the terphenyls to that of the dienes increased in the presence of air. We have noted the report[3] of the inherent instability of triphenylboron toward oxidative degradation. It seemed to us that it was possible that triphenylboron itself might play a role in the sequence of reactions occurring during the photolysis of sodium tetraphenylborate. This possibility was particularly appealing in the case where oxygen was present during the irradiations, since we had noted the formation of varying amounts of phenol in the photolysis mixtures. We decided therefore to investigate the direct photolysis of triphenylboron. The irradiations were conducted as previously described[1,2] by means of a Rayonet 2537 apparatus and in an all-quartz, water-cooled reaction vessel. When triphenylboron was irradiated in cyclohexane solution under a nitrogen atmosphere, no hydrocarbon products were found. Work-up of the irradiation mixture produced only phenol and phenylboronic acid as the products. We then concluded that in order that the hydrocarbon products be produced, the boron aryl system must be in the tetrahedral configuration to promote the "ate"-type photochemical rearrangement. To this end we carried out a study of the dependence of the absorption spectrum of solutions of triphenylboron on the nature of the solvent. When the solvent was changed from cyclohexane to ethanol, a hypsochromic shift of 6 mμ in wavelength occurred. It was also found that alcohol solutions of triphenylboron were stable at room temperature in the absence of oxygen. Brown and Dodson[3] have shown that the resistance of triarylborons toward oxygen increases with steric crowding of the aryl groups on the boron atom as one proceeds in the series triphenylboron, trinaphthylboron, and trimesitylboron. Both the attack of oxygen on triphenylboron and the formation of its amine complexes depend on the donation of an electron pair from oxygen or ammonia to the vacant orbital of the boron atom. The dependence of the wavelength of λ_{max} of absorption of triphenylboron upon the nature of the solvent indicated to us that the alcohol molecule donates an electron pair to the boron atom. Since our interest in this problem principally involved the processes which occur in the excited state, we decided to study the phosphorescent properties of triphenylboron in different media at 77°K. We have found that the wavelength of λ_{max} of phosphorescent emission of triphenylboron in the glassy state at 77°K depends on the components which make up the glass as follows (mμ): isopentane, 420; EPA, 384; isopentane–ethanol, 384; and isopentane–diethyl ether, 387. The phosphorescent emission spectrum of sodium tetraphenylborate shows its wavelength of λ_{max} of emission at 387 mμ in EPA. Sodium tetraphenylborate is not soluble in isopentane, and we were therefore unable to obtain spectra in that solvent. Irradiation of triphenylboron in methanol solution led to the formation of the desired biphenyl–diene mixtures of products but in low yields. Under similar conditions, the piperidine complex of triphenylboron yielded 32% biphenyl, 26% 1-phenyl-1,3-cyclohexadiene, 23% 1-phenyl-1,4-cyclohexadiene, and a small amount of 2-phenyl-1,3-cyclohexadiene which occurred in one gas chromatographic zone along with biphenyl. Irradiation of the pyridine complex of triphenylboron gave 63% biphenyl, 10% 1-phenyl-1,4-cyclohexadiene, 7% 3-phenyl-1,4-cyclohexadiene, and 4% 1-phenyl-1,3-cyclohexadiene.

We thus conclude that the formation of the hydrocarbon products during the photolysis of triphenylboron depends on the nature of the solvent. Solvents which donate an electron pair to the vacant orbital of the boron atom proceed *via* the "ate" photochemistry as typified by the photochemical decomposition of sodium tetraphenylborate. When complexes of amines with triphenylboron are photolyzed, "ate" photochemistry results.

The phosphorescent emission spectra were obtained in the usual manner by using a rotating-can chopper. The exciting and emitted light were modulated by means of Bausch and Lomb grating monochromators used in conjunction with an Aminco photomultiplier–microphotometer equipped with an RCA 1P21 photomultiplier tube.

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