Preparation of a New Phototropic Substance

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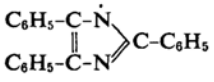
Under the investigation of the mechanism of chemiluminescence which occurred when lophine (2, 4, 5-triphenyl-imidazole) was oxidized in an ethanol solution of potassium hydroxide with an oxidizing agent, there was isolated a new phototropic substance which was considerd to be an imidazole derivative. To the solution of lophine (1 g.) in a solution of potassium hydroxide (12 g.) in ethanol (100 cc.), 450 cc. of 1% potassium ferricyanide aqueous solution was added during a period of 1.5 hr. with stirring by a stream of oxygen at room temperature. The violet color of the solution, which initially appeared, gradually disappeared and white precipitates, having a tinge of pale violet, separated out. When the oxidation was carried out in a dark place, a weak greenish blue chemiluminescence was observed. The precipitates were filtered and then washed with water repeatedly until the washing showed no reaction of ferricyanide ion. The precipitates, dried in vacuo (0.9g.) were dissolved in benzene to yield a deep red violet solution. When the solution was concentrated under reduced pressure, a lemon yellow crystalline substance separated out. It was recrystallized from ethanol as lemon yellow prisms, m. p. 199∼201°C.

Found: C, 85.20; H, 5.50; N, 9.41. Calcd. for $C_{21}H_{15}N_2$: C, 85.38; H, 5.11; N, 9.49%.

The molecular weight in benzene solution was determined to be about 290 by a cryoscopic method. Although this compound had the composition nearly equal to that of lophine, properties of these compounds were different from each other, showing that this compound was different from lophine. This compound was soluble in ordinary solvents, giving a pale yellow or almost colorless solution. Its ultraviolet absorption spectrum showed an absorption maximum at ca 267 mμ in ethanol. This compound was also obtained by the oxidation of lophine with an ethanol solution of bromine. In this case, the bromine solution was mixed in benzene with a solution of lophine in ethanolic potassium hydroxide. A mixture of ethanol solution of this compound with 4% aqueous solution of potassium ferrocyanide, which yielded white precipitates, was warmed in a water bath for 1 hr. and then water was added until white precipitates dissolved in a solution. The solution was evaporated to give white precipitates which were recrystallized from ethanol and identified to be lophine.

This compound showed a marked phototropy; when it was irradiated with sun light or light of mercury lamp in a solution of organic solvent as well as in solid at room temperature, it rapidly turned red violet, both in air and in vacuo. The absorption spectrum of the red violet solution showed absorption maxima at 350 and 550 mμ in benzene. In solid the red violet color faded slowly at room temperature but rapidly when the colored substance was warmed in a water bath. In solution the color faded rather rapidly even at room temperature. When the benzene solution of this phototropic substance was irradiated, no change of the molecular weight was observed. When nitrogen oxide gas was passed through the red violet benzene solution, the color immediately disappeared. This fact shows that the red violet coloration is due to the formation of a free radical. Electron spin resonance absorption was detected with this red violet substance in benzene solution as well as in solid⁽¹⁾. The solution of this compound exhibited thermochromism.

From the results mentioned above, it is considered that the red violet form is an oxidation product of lophine which is a free radical $C_{21}H_{15}N_2$ (I), while the lemon yellow form may be a rather labile meso ionic form.



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1) The results of the investigation by electron spin resonance absorption and spectroscopic methods will be published in the near future, T. Hayashi and K. Maeda, *J. Chem. Phys.*, in press.