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An Improved Ferrous Metal Detection Reagent

Recently the authors' laboratory reported on the use of a newly developed ferrous detection reagent [1]. This reagent, 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine-*p,p'*-disulfonic acid, disodium salt trihydrate (PDT), reacts with ferrous ion to give a magenta complex, and the reaction is sufficiently sensitive to be used to determine if an individual has recently handled a steel object such as a firearm.

We wish now to report an improved ferrous detection reagent. The reagent is not commercially available at the present time, but the efficacy of the reagent is such that the effort required for the synthesis appears justified.

The reagent PDT, as previously described, was originally intended for serum iron determinations, and the sulfonic acid groups were introduced into the molecule to render the reagent water-soluble. This, however, detracts from the value of the reagent to determine whether a person has handled a weapon. Polar, or relatively polar, solvents must be used to dissolve the PDT reagent. These solvents, for example water or methanol, cause problems in the interpretation of the pattern on the hands of a person, since the solvent runs badly. The solubility of PDT in less polar solvents is limited. The product whose synthesis and application is described here is much more soluble in nonpolar solvents and may be dissolved in acetone for spraying. The reagent is 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine, the structure of which is illustrated in Fig. 1. This compound is identical to PDT except that it does not have the sulfonic acid groups on the benzene rings.

It is necessary to comment here on nomenclature. The initialism PDT is derived from *pyridyldiphenyltriazine*. In reality, the commercial PDT is the disodium salt of the disulfonic acid derivative of PDT. The reagent described in the present article is the "true" PDT, but it cannot be referred to as PDT because in common usage PDT refers to the disulfonic salt. The writers suggest the descriptive term "pyridyldiphenyltriazine" for the reagent whose synthesis is described here.

Experimental

Reagent

The pyridyldiphenyltriazine reagent is prepared by a modification of the method of Case [2]. The synthesis is depicted in Fig. 2. A mixture of 0.05 moles of 2-cyanopyridine, 9 ml of ethanol, and 15 ml of 95% hydrazine is stirred at room temperature for 2 h. (It should be recognized that 95% hydrazine is an inherently hazardous material, and

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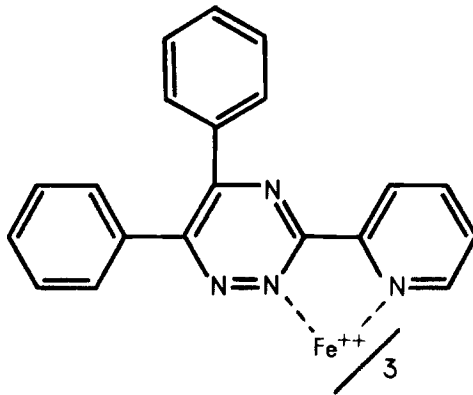


FIG. 1—Structural conformation of the planar $Fe(pyridyldiphenyltriazine)_3^{++}$ complex.

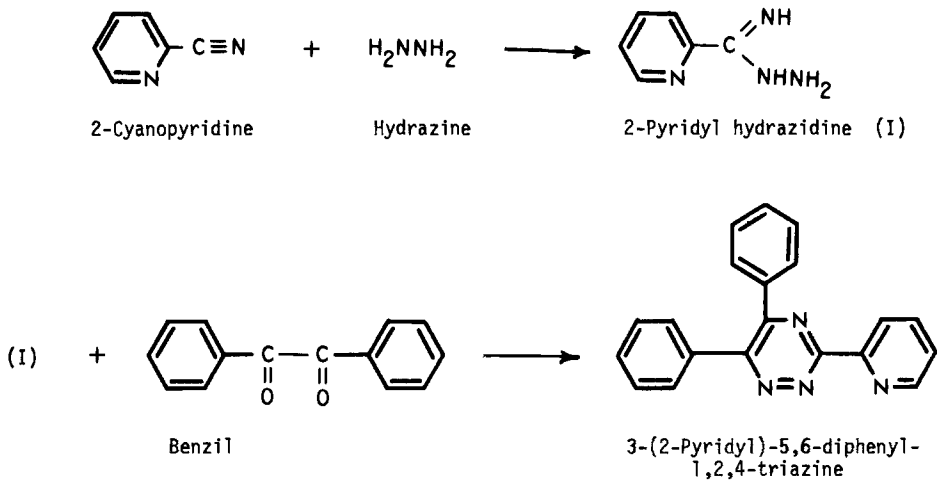


FIG. 2—Synthesis of pyridyldiphenyltriazine.

special precautions should be taken to avoid contact with the skin.) The mixture is then diluted with an equal volume of water and extracted with anhydrous diethyl ether. After removal of the ether by evaporation over a water bath, the residue (2-pyridyl hydrazidine) is recrystallized as white needles from benzene. Five millimoles of benzil are dissolved in 60 ml absolute ethanol. Five millimoles of the 2-pyridyl hydrazidine intermediate are added with vigorous stirring. After approximately 3 to 5 min a yellow precipitate begins to form. Stirring is discontinued and the solution is allowed to stand overnight. The product (pyridyldiphenyltriazine) is filtered and recrystallized as yellow needles from absolute ethanol.

Procedure

Fifty milligrams of the pyridyldiphenyltriazine are dissolved in 10 ml of acetone. The solution is sprayed over the hands of a test subject. If iron in the ferrous state is present, a magenta stain will appear instantly.

Discussion

The pyridyldiphenyltriazine reagent has two advantages over PDT as a test for ferrous iron. As previously reported [1], 10 mg of PDT may be dissolved in 10 ml of methanol. Pyridyldiphenyltriazine is much more soluble in polar solvents, however, and 50 mg of this reagent may be dissolved in 10 ml of acetone. This results in a fivefold increase in the amount of reagent that can be delivered to the skin of the test subject for an equal amount of solvent. The second advantage is related to the first. Pyridyldiphenyltriazine is quite soluble in acetone. Since a more volatile, less polar solvent is being used, the solvent evaporates rapidly, allowing for the accumulation of reagent on the skin of the subject without objectionable pooling and running of the solvent. This greatly facilitates the interpretation of the pattern developed.

The molar absorptivity of pyridyldiphenyltriazine is 24 000 at 555 nm. This is somewhat less than the molar absorptivity of 27 900 at 562 nm for PDT, but it is sufficiently high to ensure reactivity with microgram amounts of iron.

Other considerations previously outlined [1] regarding the use of iron detection reagents to determine whether a person has handled a firearm apply also to pyridyldiphenyltriazine. Information available at the present time does not indicate that pyridyldiphenyltriazine or the related PDT has a carcinogenic effect. The long-term effects of this chemical have not been fully explored, however, and caution should be taken to avoid prolonged contact or repeated exposure without adequate protection.

References

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- [2] Case, F. H., *Journal of Organic Chemistry*, Vol. 30, No. 3, 1965, pp. 931-933.

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