

PREPARATION OF PICRYL CHLORIDE¹

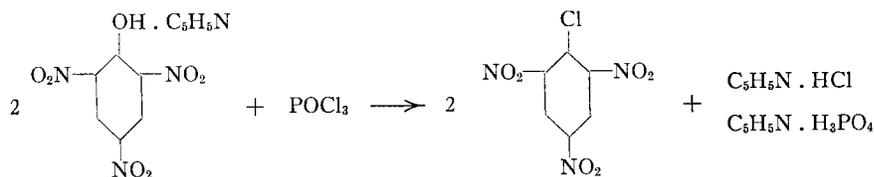
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Abstract

Picryl chloride can be prepared from pyridine picrate and either phosphorus oxychloride or phosgene in 97 to 100% yield. The pyridine used in this process is recoverable as its picrate and thus acts as a non-expended carrier during repeated preparations. Two of the chlorine atoms react in phosphorus oxychloride while only one in phosgene furnishes picryl chloride. The latter acid chloride is, however, more economical in use owing to its lower cost and molecular weight.

Picryl chloride can be prepared from one mole picric acid and two moles phosphorus pentachloride (1), but in our hands the yield was only 55% of the theoretical. The vigour of the reaction seemed to cause tar formation and to be potentially dangerous on the large scale. We modified Jackson and Gazzolo's procedure by addition of five moles of thionyl chloride and thus were able to carry out the reaction smoothly under reflux to give a 70% yield. The thionyl chloride evidently acted only as a solvent, since the use of a catalytic amount of phosphorus pentachloride in this solvent yielded no picryl chloride from picric acid. Sulphuryl chloride, phosphorus trichloride, and chlorosulphonic acid were likewise ineffective. None of these substances became reactive when catalytic amounts of benzoyl peroxide were added.

Phosphorus oxychloride also was unreactive toward picric acid alone, but we found that it reacted smoothly with pyridine picrate. Fifteen minutes' reflux in benzene solution gave a yield of good quality picryl chloride which was 98% of theoretical. Although two of the chlorine atoms in phosphorus oxychloride are available for picryl chloride formation the use of 1 : 2 ratio led to an impure product.



Practically, we have used about 0.7 moles of phosphorus oxychloride per mole of salt in order to obtain a 98% yield of good picryl chloride melting at 79° to 81° C.

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In the event that a considerable quantity of picryl chloride were needed, the process could be made both convenient and economical. The soluble pyridine salts, which remain in the aqueous liquors used to wash the benzene solution, may be precipitated by addition of picric acid to the warm aqueous liquors. This regenerated pyridine picrate (93% recovery) is entirely adequate for a subsequent preparation.

The reaction between picric acid and phosphorus pentachloride yields phosphorus oxychloride. Since both of these phosphorus halides are priced the same in quantity lots, it may be calculated stoichiometrically that a slight advantage in quantity manufacture would result by initial use of phosphorus pentachloride on picric acid, followed by recovery of the phosphorus oxychloride for subsequent utilization with pyridine picrate. This stepwise operation would be necessitated by the fact that phosphorus pentachloride (as well as phosphorus trichloride, sulphuryl chloride, and chlorosulphonic acid) will not react with pyridine picrate, although it will react with picric acid.

All such speculation respecting economical production of picryl chloride from the phosphorus halides was, however, cut short by the discovery that phosgene, which was unreactive toward picric acid at 100° C. during three hours' contact, reacted quantitatively with pyridine picrate. The salt was treated in an autoclave for two hours at 56° C. with 50% or greater excess of phosgene to give a 100% yield of crude picryl chloride melting at 79° to 80° C. This crude was the residue obtained by atmospheric evaporation of the recoverable phosgene followed by aqueous wash to remove the pyridine hydrochloride. Although only one of the chlorine atoms in phosgene is available for picryl chloride formation, the chloride affords a cost advantage of at least 20% over the process using phosphorus halides.

Most of our work was carried out in low pressure autoclave equipment, but it was found that 97% yield could be effected by condensing phosgene into pyridine picrate at 0° C. After one-half hour, the excess of phosgene was evaporated at room temperature and the residue washed with water to remove the recoverable pyridine hydrochloride.

The pyridine picrate used initially in this process was prepared in 98% yield by combination of the ingredients in ethanol. The salt, melting at 166° C., was much easier to filter than that prepared in aqueous solution from equivalent amounts of hot aqueous sodium picrate and pyridine hydrochloride. The melting point of this cheesy precipitate, 242° C., was unaffected by resolution and recrystallization from its own mother liquors or from ethanol, but when crystallized from pure water it melted at 166° C. When technical pyridine (average molecular weight of 107 in contrast to pyridine of 79) was used instead of pure pyridine for preparation of the salt, the precipitate melted at 88° to 153° C. as might be expected of a mixture of salts. This impure picric acid salt was, however, equally effective in picryl chloride preparation with that derived from pure pyridine.

The recovery of pyridine from the products prepared from phosphorus oxychloride was effected by precipitating calcium phosphate from the aqueous

liquors used to wash the benzene solution of picryl chloride. After this treatment with an excess of lime, picric acid was added to the hot stirred filtrate until precipitation of pyridine picrate was complete. The lime treatment was, of course, not necessary when phosgene was used as the acid chloride. In either case the pyridine picrate was thoroughly air-dried before re-use.

Although the crude products from these preparations are not pure picryl chloride, which melts at 83° C., they are adequate for many uses. Thus this crude picryl chloride could be converted in 99% yield to N-methylpicramide, which in turn was pure enough that it could be converted in 97% yield to pure tetryl.

Experimental*

Preparation of Pyridine Picrate

Method 1.—To a solution of 22.9 gm. (0.1 mole) picric acid in 200 cc. of hot 95% ethanol was added 7.9 gm. (0.1 mole) of pyridine. A 98% yield (30.1 gm.) was filtered off the cooled solution. The salt melted at 166° C.

Method 2.—To a solution of 22.9 gm. (0.1 mole) of picric acid dissolved in 200 cc. of hot 2% aqueous sodium hydroxide was added 7.9 gm. (0.1 mole) of pyridine in 28.6 cc. of dilute hydrochloric acid. A cheesy precipitate, difficult to filter, was obtained on cooling. It weighed 28.1 gm. (91% of theoretical) and melted at 242° C. This melting point was unchanged after crystallization from ethanol or from the precipitating liquors but water recrystallization converted it to the ordinary pyridine picrate melting at 166° C.

Picryl Chloride from Phosphorus Oxychloride

One mole (308 gm.) of dry pyridine picrate was boiled for 15 min. under reflux with 0.67 mole (103 gm.) of phosphorus oxychloride in 250 cc. benzene. Both the precipitated oil and the benzene layer were washed several times with hot water. The benzene solution on evaporation yielded 73% of the theoretical amount of picryl chloride while the residue from the precipitated oil constituted 25% of the theoretical yield. The total (98% yield) picryl chloride melted at 79° to 81° C.

The aqueous washing liquors were treated with an excess of hydrated lime to remove phosphate. After filtration the solution was heated to 70° C. and stirred while one mole (229 gm.) of picric acid was added slowly to insure solution. The pyridine picrate that precipitated completely on cooling melted at 166° C. and weighed 298 gm. or 97% of theoretical. This was air-dried before re-use together with the evaporated benzene.

Picryl Chloride from Phosgene

Into one mole (308 gm.) of dry pyridine picrate in a light iron pressure vessel or bomb tube was poured or condensed 1.5 moles (148.5 gm.) of commercial phosgene. After two hours or less at 56° C. the pressure was released to distil off the excess phosgene. The remainder was blown with air to remove

*All melting points are corrected.

last traces of poisonous gas and was then ground in a mortar with three 500 cc. portions of water at 70° C. The remaining picryl chloride weighed 247 gm. (100% yield) and melted at 78° to 79.5° C.

The combined aqueous wash liquors were heated to 70° C. and stirred while 1 mole (229 gm.) of picric acid was added slowly. After cooling to complete precipitation the pyridine picrate was filtered off and air-dried to weigh 287 gm. or 93% of the amount originally added. Either quinoline or the mixture of pyridine, picolines, and lutidines known as "technical pyridine" works as satisfactorily except that filtration of the recovered pyridine salts is slightly more difficult.

This method of picryl chloride preparation may be varied by eliminating the heating period at 56° C. After the phosgene was poured or condensed into the pyridine picrate at 0° C., the mixture was let stand at this temperature for 30 min. and then warmed to 25° C. to remove the phosgene. The yield of picryl chloride, m.p. 78° to 79° C., from an otherwise identical procedure was 96.7% of theoretical. The yield was, however, decreased to 50% or less when gaseous phosgene was passed over thin layers of pyridine picrate either at 25° or 55° C. for 30 min.

Preparation of N-methylpicramide

The method of van Romburgh (2) was followed by adding 0.024 mole (0.74 gm.) of methylamine in 4 cc. methanol to 0.01 mole (2.47 gm.) of crude picryl chloride, m.p. 78° to 79.5°, in 3 cc. methanol at 20° C. The crystals were filtered off and washed once with methanol. The combined methanolic solutions were evaporated and the crystal crop recrystallized from benzene. In this manner a 99.2% yield (2.40 gm.) of N-methylpicramide, m.p. 110° to 110.5° C., was obtained.

Preparation of N-methyl-N-nitropicramide (Tetryl)

Treatment of 0.0025 mole (0.61 gm.) of N-methylpicramide, m.p. 110° to 110.5°, with 0.06 mole (4 cc.) of 70% nitric acid, followed by evaporation on the steam-bath gave a yellow residue. When this was water-washed and dried it represented a 97.0 yield of tetryl melting at 128° to 129° C.

References

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