

## PREPARATION OF PICRAMIDE<sup>1</sup>

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### Abstract

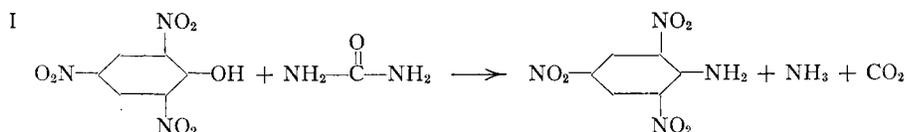
The method of Kym for conversion of phenols into aromatic amines has been applied to picric acid. An 88% yield of picramide has been obtained by adjusting the reaction temperature to 173° C., the molar urea : picric acid ratio to 3 : 1, and the reaction time to 36 hr.

In connection with the preparation of tetranitrobenzene (2), we required a cheap, plentiful, and safe method for obtaining the necessary picramide. The method of Merz and Ris (4), which involves the action of 35% ammonia on nitrophenols to give aminonitrobenzenes, gave a charcoal-like product with picric acid after 16 hr. at 160° to 170° C. A control experiment involving picramide instead of picric acid under the same conditions showed that 88% of the picramide was recoverable and therefore would not have been destroyed under this reaction environment. Similarly no picramide could be obtained from picric acid and zinc chloride ammoniate ( $ZnCl_2 \cdot 2NH_3$ ) at 155° C., although a comparable experiment with picramide showed no degradation.

Kym (3) has reported that nitrophenols can be converted to aminonitrobenzenes by heating the phenol with urea. Thus he obtained a 75% yield of 2,4-dinitroaniline from one part of 2,4-dinitrophenol and three parts (9.2 moles) of urea at 208° C. for eight hours. We found that this method was applicable to the preparation of picramide.

Our first experiments were carried out for seven hours at 155° C. using Kym's 9.2 molar ratio of urea to picric acid. The 12% yield could be increased to 26% by increasing the reaction time to 16 hr. A further yield increase to 45% was effected by raising the temperature to 173° C. and this was augmented to 67% by reducing the molar urea-picric acid ratio to 4.5.

The reaction produces ammonia and ammonium carbonate as might be expected from Equation (I),



and on this basis an excess of urea would seem to be unnecessary. However, a water and acetone-insoluble by-product is formed which must arise by decomposition of the urea. This alternative consumption of urea may account for

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the fact that a low yield, chiefly ammonium picrate, was obtained when equimolar quantities of picric acid and urea were heated 16 hr. at 173° C. Two moles of urea per mole of picric acid was still not sufficient to supply reagent for both main and side-reactions, since a yield of 15% picramide was optimum under these conditions. The use of three moles of urea seemed, however, to supply an adequate excess.

This 3 : 1 molar ratio of urea to picric acid produced 73% of picramide in 13 hr. Time of reaction, and not further excess of urea, was shown to be the limiting yield factor by evaporating to dryness the water-washing liquor from this latter picramide yield and then reheating aliquots of the residue for 24 hr. longer, with and without additional urea. A further 12% yield was obtained in either case. This finding was substantiated by a complete experiment wherein three moles of urea per mole of picric acid was heated 36 hr. at 173° C. to give an 88% yield of picramide melting at 187° to 188° C. A slightly higher (91%) yield of poorer product (m.p. 185° to 189° C.) was obtained at a reaction temperature of 183° C.

The fate of the reagents is shown in the following capitulation of this latter experiment.

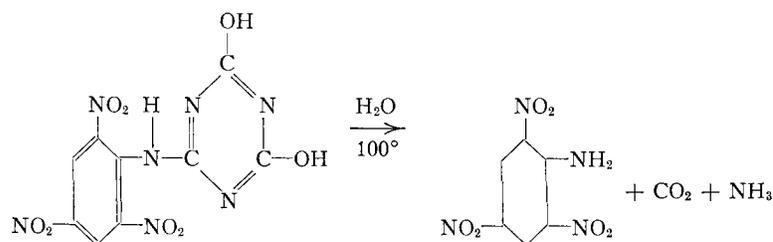
	Grams	Moles	Weight, gm.	Moles
Reagents:				
(Picric acid)	229	1		
(Urea)	180	3		
Products:				
Water soluble (urea)			31.8	0.53
Sublimate (ammonium carbonate by titration)			70.2	0.73
Gas evolved (ammonia by titration)			5.7	0.33
Picramide (m.p. 185°-189°)			207.7	0.91
Acetone-insoluble (as derivatives of cyanic acid)			63.2	1.47 (as cyanic acid)
(as "bound" picramide)			15.8	0.07
Total recovered			394.4	

This 96% material recovery affords some insight into the fate of the urea and the course of the reaction, although a thorough knowledge could be realized only by complete analysis of the acetone-insoluble material.

This analysis is not complete. Extraction with boiling water yields 25% of its weight as cyanuric acid. When the remainder is boiled with 600 parts of water, ammonia is produced, together with a small amount of cyanuric acid. The poorly crystalline material which precipitates on cooling represents 23% of the total; this material yielded 90% of its weight as pure picramide when it was extracted with acetone. Neither picric acid, melamine nor biuret could be detected.

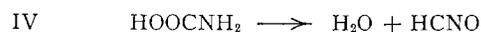
This indicates that about 75% of the acetone-insoluble material is a condensation product of picrylurea. Although the solubility of the acetone-insoluble material in alkali would indicate that this might be picrylammelide,

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the material must necessarily be more complex in order to account for the limited weight of picramide that is recovered after its decomposition. Further speculation seems fruitless until some means can be found to characterize further this intractable material. It must at present be considered a material bound by urea decomposition products from which, by boiling, sufficient picramide can be recovered to bring the total yield of the latter substance to 98% of the theoretical amount. It probably is significant that with increasing ratio of urea to picric acid the yield of acetone-soluble (free) picramide *decreased* while the amount of acetone-insoluble material increased.

The material balance (1 picramide: 1.79 NH<sub>3</sub> : 0.73 CO<sub>2</sub>) shows, either that part of the carbon dioxide product according to Equation (I) is utilized in urea condensation, or, more probably, that the reaction follows an alternate course:



while the ammonia, ammonium carbonate, and the remainder of the cyanic acid involved in the acetone-insoluble material are derived by decomposition of urea. Such formulations are, of course, subject to urea decomposition equilibria at temperatures below 200° (5), nor is the intermediate formation of urea picrate and picrylurea excluded.

### Experimental\*

#### Picramide

One mole of picric acid melting at 120° to 121° C (229 gm.) was mixed with three moles (180 gm.) of technical urea in a 1 litre distilling flask equipped with a side-arm of 20 mm. diameter. The effluent from the receiver was passed through standard acid. At the end of the experiment both the ammonium carbonate in the receiver and the ammonia absorbed in the acid were estimated independently. The reaction flask neck was equipped with a thermometer with bulb immersed in the reagents.

\* Melting points corrected against known standards.

The reaction flask was suspended with its equator 4 to 5 inches below the lip of a 3 litre beaker. Above the equator was coiled copper tubing to act as a condenser, and the flask neck was surrounded with a loosely fitting lid to eliminate bath losses owing to draughts. The beaker was filled about 1 inch in depth with *o*-dichlorobenzene (b.p. 183° C.) or a mixture of this with *p*-dichlorobenzene in case a lower temperature such as 173° C. was desired. A bare nichrome heating coil (250 watt) was immersed in the dichlorobenzene.

After 36 hr. reflux the flask content was removed from the flask with 1500 cc. water at 40° C. The aqueous washings were concentrated and the amount of recovered pure urea (m.p. 130° to 165° C.) was determined in this concentrate by dry weight. The water-insoluble portion of the reaction mixture was eluted with 2,000 cc. acetone in a Soxhlet extractor. The picramide was recovered from this acetone solution by evaporation of the solvent to weigh 207.7 gm. (91% of theoretical) and melt at 185° to 189° C. Further purification from acetone raised this melting point to 188° to 189° C. with a recovery of 88%.

The brown acetone-insoluble product dissolved, for the most part, slowly in 20 to 30% alkali to yield, after 20 hr., the insoluble crystalline trisodium cyanurate. Alternatively 25% of the acetone-insoluble material could be recovered as cyanuric acid by five-minute extraction with 25 parts of boiling water. This compound was identified by its crystal form, its loss of solvate water on heating to 56° (15 mm.) and by the titrimetric conversion of its trisodium salt to the disodium salt using phenolphthalein as indicator (1).

A 2.18 gm. aliquot of the cyanuric acid-free acetone-insoluble material was boiled one hour with 600 parts of water and filtered hot. The precipitate that appeared on cooling was filtered off, dried, and 0.5 gm. was boiled for 30 min. with 25 ml. acetone. The filtered solution was evaporated under 15 mm. to yield 0.43 gm. of picramide, m.p. 188° to 189° C. This melting point was not depressed by admixture of the product with an authentic sample.

### References

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