[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF QUEENS COLLEGE]

Replacement of Halogen by Hydrogen in Nitro Aryl Halides[1]

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The preparation of picryl iodide is described. HI and H_3PO_2, either together or separately, will reduce picryl iodide to trinitrobenzene. The reduction with HI is kinetically complex.

Some time ago we reported that picryl chloride was converted to trinitrobenzene on treatment with dilute hydriodic acid in an organic solvent at room temperature, *i.e.*, under the conditions that bring about the reduction of an α-halo ketone to a ketone.[2]

$$2,4,6\text{-}(O_2N)_3C_6H_2Cl + 2HI \longrightarrow 1,3,5\text{-}(O_2N)_3C_6H_3 + HCl + I_2$$

We have since undertaken a study of the mechanism of the reaction and of its usefulness. Our experiments designed to establish the mechanism have not led to clear cut results, but they have resulted in a number of findings of considerable interest. These by-product findings constitute the subject matter of this article.

In order to reduce the number of problems involved in the study of mechanism, we decided to examine first the reaction between picryl iodide and hydriodic acid as that would eliminate complications resulting from the reaction between picryl chloride and iodide ion to furnish picryl iodide and would also simplify the stoichiometry:

$$2,4,6\text{-}(O_2N)_3C_6H_2Cl + I^- \longrightarrow 2,4,6\text{-}(O_2N)_3C_6H_2I + Cl^-$$

$$2,4,6\text{-}(O_2N)_3C_6H_2I + HI \longrightarrow 1,3,5\text{-}(O_2N)_3C_6H_3 + I_2$$

For this purpose it was necessary to prepare picryl iodide and in the course of this preparation we were able to develop what promises to be a useful qualitative test for aromatic nitro compounds and the number of nitro groups they contain.

The only practical method for preparing picryl iodide is the reaction between picryl chloride and an alkali iodide, but the only description of this reaction lacks essential details and did not give satisfactory results when we tried to follow it.[3] In part at least the difficulty is probably a consequence of the reaction between picryl chloride and the solvent, ethanol, to yield picryl ethyl ether and hydrogen chloride, for the hydrogen chloride with potassium iodide would furnish hydriodic acid and this would lead to reduction to trinitrobenzene and oxidation to iodine.[4] By changing to acetone as the solvent and sodium iodide as the inorganic reagent it was possible to repress the side reactions and increase the concentration of reactants sufficiently to prepare the picryl iodide we needed.

In our first trial of the reaction between picryl chloride and sodium iodide in acetone we noticed, on mixing the solutions of the reactants, the development of an intense color comparable with that of liquid bromine. A series of test-tube experiments showed that the color was not specific for the reactants and products present or for the reaction taking place, and that similar or related colors developed whenever an aromatic nitro compound and iodide ion were together in acetone. When equal volumes of approximately 0.2*M* acetone solutions of sodium iodide and an aromatic nitro compound are mixed, the resulting solution will be very pale yellow if the aromatic compound contains one nitro group; deeper yellow, comparable with the color of 0.3*M* aqueous ferric chloride if the aromatic compound contains two nitro groups; and red brown, comparable with the color of 3.0*M* aqueous ferric chloride, if the aromatic nitro compound contains three nitro groups. Exact concentrations of reagents are not necessary, for on diluting with acetone a solution containing a trinitro aromatic compound and iodide ion the red-brown color becomes less intense but is still readily distinguished from the yellow color that characterizes a dinitro aromatic compound. An alkyl, hydroxyl, amino, carboxyl, or carbalkoxyl group or a halogen atom as a substituent modifies the color (*e.g.*, the color developed by picric acid is more brown and less red than that developed by trinitrobenzene), but these groups do not interfere with the use of the test to show the number of nitro groups present. The nitroso groups in *o*-dinitrosobenzene and in 3,5-dinitro-1,2-dinitrosobenzene likewise do not interfere; the first-named compound does not develop a color while the last-named compound behaves like other dinitro aromatics.[5] The aliphatic nitro compounds, nitromethane and 2-nitro-2-methylpropane, do not develop

(1) This work has been supported by the Office of Ordnance Research under Contract No. DA-30-069-ORD-1289.

(2) A. H. Blatt and E. W. Tristram, *J. Am. Chem. Soc.*, **74**, 6273 (1952).

(3) P. Hepp, *Ann.*, **215**, 361 (1882).

(4) The reaction between picryl chloride and ethanol is reported to be very fast: C. K. Ingold, *Structure and Mechanism in Organic Chemistry*, p. 804, Cornell University Press, Ithaca, N. Y., 1953. Apparently no detailed information on the reaction has been published.

(5) We are indebted to Dr. J. H. Boyer for this information.

colors.[6] Cyclotrimethylenetrinitramine (RDX) and pentaerythritol tetranitrate (PETN), examined as representative of nitramines and nitrate esters, also fail to develop colors with iodide ion.[7]

A much wider range of aromatic nitro compounds will, of course, have to be examined before the usefulness and limitations of this color test can be closely defined. We are trying additional compounds as they come to hand. So far we have found that 1,5- and 1,8-dinitronaphthalene, representative of fused ring aromatics, behave like typical dinitrobenzene derivatives; that 2,2′-dinitrobiphenyl at 0.2*M* behaves like a mononitrobenzene derivative at roughly 0.4*M*, and that 2,4,5-trinitro- and 2,4,5,7-tetranitrofluorenone develop deep purple colors like that of moderately concentrated aqueous potassium permanganate.

The colored complexes from aromatic nitro compounds and iodide ion are destroyed by the addition of water. From the one complex whose acetone solution we examined in a little more detail, that from *m*-dinitrobenzene, it was possible to recover the aromatic nitro compound essentially quantitatively after 24 hours by pouring the solution into water. We have found only one report of these colored complexes. In that report three trinitro- and two dinitrobenzene derivatives were examined, the solvent and inorganic halide were varied widely, and it was concluded that the complexes were probably composed of one molecule of aromatic nitro compound, one molecule of alkali iodide, and three molecules of solvents.[8] We do not propose to study the complexes themselves; they form the subject matter of a recent note in this Journal.[8a]

With picryl iodide available, we undertook to secure kinetic data on the reaction between it and hydriodic acid. Preliminary experiments showed that 0.56*M* picryl iodide and 0.113*M* hydriodic acid in acetone containing 9.6% water gave convenient rates and gross reproducibility for the early stages of the reaction when it was run in a nitrogen atmosphere in flasks covered with aluminum foil to exclude light. The careful follow-up of these preliminary experiments did not, however, increase their reproducibility sufficiently to permit their use for the calculation of reaction rate and order. The principal source of trouble was the decomposition of the hydriodic acid. Along with each pair of runs we ran a blank to which no picryl iodide had been added. After correcting for the iodine liberated in the blank, the two runs would usually agree to within a per cent or two on the amount of reduction that had taken place during forty minutes. However, the amount of iodine formed in the blanks was so large and so variable–amounting to from 12 to 22% of the total iodine formed in the reaction proper–that it was not safe to assume that the blanks were a reliable measure of the decomposition of the hydriodic acid in the reaction mixtures.

We next tried a number of variations in the experimental procedure in the hope of obtaining a more closely reproducible reaction. None of the variations was successful for the purpose for which it was intended, but several yielded interesting and significant information. The addition of sodium or potassium acetate in amount equivalent to the hydriodic acid present repressed in striking fashion the decomposition of the hydriodic acid but did not increase the reproducibility of runs sufficiently for our purpose, indicating that there were other variables in the system. Details of the inhibiting effect of sodium acetate on the decomposition of hydriodic acid are given in the experimental section for the information of any one who may want to make use of or to study it.

The results just described suggested the use of equivalent amounts of sodium iodide and acetic acid in the hope that this reagent combination would have the stability of the hydriodic acid-sodium acetate system and would eliminate any interfering species present in hydriodic acid. When the experiment was made we found that, under conditions such that hydriodic acid and sodium acetate gave 5% reduction in 40 minutes, sodium iodide and acetic acid gave only 1% reduction in the same time. The discrepancy was finally traced to the small amount of hypophosphorous acid (~1%) present as a stabilizer in commercial hydriodic acid and, with this lead, it could be shown that hypophosphorous acid alone is the most effective and convenient reagent for the reduction of picryl iodide to trinitrobenzene. With this reagent the reduction is quantitative and rapid at room temperature. The use of hypophosphorous acid for this type of reduction is, as far as we can find, new. We write the reaction in the following way which takes into account our observations that the other *ous* acids, phosphorous and sulfurous, also bring about the same reduction:

$$2,4,6\text{-}(O_2N)_3C_6H_2I + H_3PO_2 + H_2O \longrightarrow 1,3,5\text{-}(O_2N)_3C_6H_3 + H_3PO_3 + HI$$

$$2,4,6\text{-}(O_2N)_3C_6H_2I + H_3PO_3 + H_2O \longrightarrow 1,3,5\text{-}(O_2N)_3C_6H_3 + H_3PO_4 + HI$$

$$2,4,6\text{-}(O_2N)_3C_6H_2I + H_2SO_3 + H_2O \longrightarrow 1,3,5\text{-}(O_2N)_3C_6H_3 + H_2SO_4 + HI$$

We are studying the hypophosphorous acid reaction further and hope to be able to report on it in more detail later.

After hypophosphorous acid had been shown to be capable of reducing picryl iodide, we tried unstabilized hydriodic acid. Both the commercially available material as received and the freshly dis-

(6) We are indebted to Dr. Nathan Kornblum for the information about 2-nitro-2-methylpropane.

(7) We are indebted to the General Laboratory Section, Picatinny Arsenal, for this information.

(8) B. Tronow, L. Djakanowa-Schulz, and E. Sonowa, *J. Russ. Phys. Chem. Soc.*, **59**, 333 (1927) [*Chem. Abstr.*, **22**, 2555 (1928)].

(8a) Richard W. Shellman, *J. Org. Chem.*, **22**, 818 (1957).

tilled material gave reasonably consistent results for a given sample. However, the results varied widely from sample to sample and were therefore of no value to us.

The conclusion from the experiments so far described is that the reaction between picryl iodide and hydriodic acid is in our hands not amenable to kinetic study; hydriodic acid stabilized with hypophosphorous acid contains at least two reducing species; sodium iodide and acetic acid reduce picryl iodide too slowly; and unstabilized hydriodic acid, judging from the variations between different samples, also contains more than one reducing species. However, the rough quantitative measurements of the amount of picryl iodide reduced under a number of different experimental conditions and of the amounts of other nitro aryl halides reduced under a standard set of conditions do give practical information about the best way to carry out the reduction and about the applicability of the reaction.

With picryl iodide as the substrate in acetone and with hydriodic acid stabilized with hypophosphorous acid as the reagent, reduction is strikingly inhibited by water. Reduction is faster in acetic acid than in acetone. (The solubility of picryl iodide in aqueous acetic acid is too small for us to determine whether water is also an inhibitor in this solvent.) Supporting data are in Table I. The obvious practical

TABLE I

REDUCTION OF PICRYL IODIDE TO TRINITROBENZENE IN 40 MINUTES AT 24.2°

Picryl iodide, 0.056*M*. Hydriodic acid (stabilized with ~1% H_3PO_2), 0.112*M*

Solvent	Per Cent Reduction
Acetone containing 9.6% water	5.5
Acetone containing 5.6% water	12–13
Acetone containing 1.66% water	76–77
Acetic acid containing 1.66% water	98–99

conclusions are confirmed by separate preparative experiments showing that 0.056*M* picryl iodide in acetone containing 1.66% water and four equivalents of hydriodic acid or in acetic acid containing 1.66% water and two equivalents of hydriodic acid is quantitatively reduced to trinitrobenzene in 40 minutes at room temperature.

Just as striking as the effect of water on the reduction of picryl iodide with stabilized hydriodic acid, is the effect of acidity on the reduction with hydriodic acid formed from sodium iodide and an added acid. Thus, under conditions such that sodium iodide and an equivalent amount of acetic acid in acetone brought about only 1% reduction of picryl iodide, sodium iodide and an equivalent amount of hydrochloric acid brought about essentially complete reduction to trinitrobenzene. The dependence of reduction on acidity enables one to control the course of the reaction between picryl chloride and hydriodic acid so as to yield either picryl iodide (in weakly acid solution) or trinitrobenzene (in strongly acid solution). Sodium iodide and an equivalent of acetic acid is the best reagent combination for the preparation of picryl iodide from picryl chloride. It remains to be seen whether the sodium iodide-acetic acid reagent is generally superior for the conversion of nitro aryl chlorides and bromides to the corresponding iodides and how this reagent compares with an alkali iodide alone in the formally analogous conversion of alkyl chlorides and bromides to iodides.

Considering now the behavior of other nitro aryl halides than picryl iodide toward stabilized hydriodic acid under a standard set of conditions (nitro aryl halide, 0.056*M*; hydriodic acid, 0.112 *M*; in acetone containing 1.66% water at 24.2°), we find that in the benzene series three nitro groups are necessary in order for reduction to take place. Picryl bromide and picryl chloride are reduced to trinitrobenzene, both more slowly than picryl iodide and the chloride more slowly than the bromide. The 2,4-dinitrophenyl halides (X = F, Cl, Br, I) are not reduced. Neither is 2,6-dinitroiodobenzene. A carbomethoxyl group will not effectively replace a nitro group in picryl chloride; the methyl esters of 2-chloro-4,6-dinitrobenzoic acid and 4-chloro-2,6-dinitrobenzoic acid are not reduced. Replacement of halogen by hydrogen is therefore of quite limited applicability in the benzene series. However, in the thiophene series two nitro groups are sufficient to permit reduction for 2-bromo-3,5-dinitrothiophene is reduced to 2,4-dinitrothiophene. This result suggests that the reduction may have wider application in suitable heterocyclic systems. We have begun a study of these applications and our results in the thiophene series are described in the accompanying article.[9]

EXPERIMENTAL

All acetone used was refluxed over potassium hydroxide and permanganate, distilled, and then redistilled over permanganate through a 24″ glass-packed column shortly before use. Other solvents were purified by standard procedure and distilled through the same column. Picryl chloride was crystallized from formic acid; picryl iodide was crystallized from benzene.

Preparation of picryl iodide. The bulk of the picryl iodide used was prepared in the following way. Fifty grams (0.2 mole) of picryl chloride was dissolved in 175 ml. of acetone, and 45 g. (0.3 mole) of Baker's Analyzed Reagent sodium iodide was dissolved in 125 ml. of acetone with cooling. The solutions were mixed and kept stoppered for 8 hr. protected from light. Immediately on mixing, the solution developed a deep red-brown color like that of liquid bromine and in a few minutes a precipitate, presumably sodium chloride, began to form. The reaction mixture was poured into 1.7 kg. of water containing a small amount of ice. The brown precipitate was allowed to coagulate for an hour and was then filtered from the red-brown solution. The crude prod-

(9) A. H. Blatt, Norma Gross, and E. W. Tristram, in press.

uct weighed 60 g. and melted at 138–152° after softening from 125° on. It was dissolved in 180 ml. of benzene, filtered, and concentrated to 60 ml. On cooling the solution, 39 g. (57%) of picryl iodide, melting at 161–163° with some preliminary softening, was obtained. A second crystallization from benzene was necessary to obtain a pure product. The filtrate from the first crystallization, on evaporation to dryness at room temperature, left 20 g. of solid melting over the range 60–90°. We were unable to separate this material into its constituents.

Occasional runs by the procedure just described, and by a variation of that procedure using shorter reaction times, gave products that did not coagulate satisfactorily. When this happened, the yield of picryl iodide was poor and there were indications of the intrusion of side reactions. One indication was the presence of a lachrymator (iodoacetone ?) in the reaction mixture; another was the formation of unidentified material that melted above 200°. We did not attempt to identify these side reactions or their products for we found that they could be avoided by operating in weakly acid solution in the following way.

A solution of 12 g. (0.08 mole) of sodium iodide in 50 ml. of acetone was added to a solution of 10 g. (0.04 mole) of picryl chloride in 25 ml. of acetone and 5 ml. of anhydrous acetic acid. The reaction mixture immediately developed a dark red color and in a few minutes a precipitate formed. After 30 min. the reaction mixture was poured into 340 ml. of water in which 0.1 g. of sodium bisulfite had been dissolved. The color disappeared and picryl iodide precipitated as a pale yellow solid. The crude product weighed 11.0–11.5 g. (80%) and melted over the range 130–148°. One crystallization from benzene furnished picryl iodide suitable for most purposes, but the material was crystallized a second time for use in quantitative experiments. The yield was comparable with that obtained in the absence of acid.

Reduction of picryl iodide to trinitrobenzene. A. Quantitative measurements. Little need be added to the description given in the discussion earlier. The course of the reaction was followed by titrating with thiosulfate the iodine formed. A check on the titrations could be made when reduction was very slight or was essentially complete by isolating the product and determining the melting point.

B. With hypophosphorous acid. To 1.0 g. (0.003 mole) of picryl iodide in 25 ml. of acetone, 2 ml. (0.019 mole) of 50% hypophosphorous acid was added. The reaction mixture rapidly developed a deep red color. After 2 hr. the solution was poured into 160 ml. of water. The precipitate of trinitrobenzene weighed 0.45 g. and melted at 118–120°. The yield was 75%; corrected for the recovery of trinitrobenzene when 0.6 g. of that material is dissolved in 25 ml. of acetone and the solution poured into 150 ml. of water, the yield is better than 95%.

Colored complexes from aromatic nitro compounds and sodium iodide. Our procedure for these tests is to add to an approximately 0.2*M* acetone solution of the aromatic nitro compound an equal volume of an approximately 0.2*M* stock solution of sodium iodide. About 0.2 g. of the nitro compound, enough to make 1 or 2 ml. of solution, is used. It is weighed to about ±0.03 g. The following nitro aromatic compounds have been tried with the results described in the discussion above.

A. Mononitro compounds: Nitrobenzene, *p*-nitrotoluene.

B. Dinitro compounds: *o*- and *m*-Dinitrobenzene, the 2,4-dinitrohalobenzenes (X = F, Cl, Br, I), 2,6-dinitroiodobenzene, 2,6-dinitroaniline, 3,5-dinitrobenzoic acid, methyl 2-chloro-4,6-dinitrobenzoate, methyl 4-chloro-2,6-dinitrobenzoate, 1,5- and 1,8-dinitronaphthalene.

C. Trinitro compounds: 1,3,5-Trinitrobenzene, TNT, picric acid, 2,4,6-trinitrobenzoic acid, picryl chloride, bromide, and iodide.

2,4,7-Trinitro- and 2,4,5,7-tetranitro-fluorenone gave deep purple solutions, while 2,2′-dinitrobiphenyl at 0.2*M* behaved like a mononitro aromatic at about 0.4*M*.

Stabilization of hydriodic acid by sodium or potassium acetate. Samples of hydriodic acid were diluted with water or acetone until 5.56 millimoles of hydriodic acid was present in 50 ml. of solution. The solutions were analyzed for iodine by titration with thiosulfate (a) immediately or shortly after they had been prepared and (b) after they had been left standing for varying lengths of time in glass stoppered flasks. The results are given below as the per cent of hydriodic acid decomposed and, in parentheses, as the millimoles of iodine found per 5.56 millimoles of hydriodic acid originally present:

	Per Cent of Hydriodic Acid Decomposed (Millimoles of Iodine Present)		
	Initially		After 2 months
Commercial hydriodic acid diluted with acetone	3% (0.09)		50% (1.5)
As above with one equivalent of CH_3CO_2Na added	3% (0.08)		15% (0.4)
	Initially		After 20 Days
Commercial hydriodic acid freshly distilled in carbon dioxide atmosphere and diluted with water	1.5% (0.04)		25% (0.71)
As above with one equivalent of CH_3CO_2Na added	0.5% (0.01)		4% (0.1)
As above with one equivalent of CH_3CO_2K added	0.4% (0.01)		4% (0.1)
	After 30 min.	After 60 min.	After 24 hr.
Commercial hydriodic acid stabilized with H_3PO_2, diluted with acetone	2% (0.05)	7% (0.09)	54% (1.5)
As above with one equivalent of CH_3CO_2Na added	0.4% (0.01)	0.4% (0.011)	4% (0.1)
As above with one equivalent of CH_3CO_2K added	0.3% (0.007)	0.4% (0.012)	4% (0.1)

The addition of less than one equivalent of sodium or potassium acetate also inhibits the decomposition, but less effectively.

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