β-I) (2.0 g., 0.0062 mole) was treated in the same manner as *dl*-α-I above. The yield of crude *dl-cis*-III was 1.6 g. (85%) which after recrystallization from ethanol melted at 86–87°. A mixed m.p. with *dl-cis*-III prepared above showed no depression.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF GEORGIA]

The Action of Silver Picrate on Alkyl Halides

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The synthesis of alkyl picryl ethers by the method of Stenhouse and Muller has been studied and extended to the preparation of seven alkyl picryl ethers. Isopropyl and *n*-butyl picryl ethers have been prepared for the first time. The effect of the nature of the alkyl group on these reactions has been studied. Silver picrate has been found to dehydrohalogenate alkyl iodides under mild conditions and the production of picric acid in these reactions has been explained. The method of Bird for the synthesis of these compounds has been re-examined.

The production of ethyl picryl ether from silver picrate and ethyl iodide was first reported by Stenhouse and Muller.[2] These authors observed that picric acid was the major product of this reaction unless large excesses of ethyl iodide were used. Picric acid was the main product also when ethyl alcohol was present as a solvent. The method was applied by Holleman[3] to the preparation of methyl picryl ether from methyl iodide, and by Meisenheimer[4] to the preparation of isobutyl picryl ether.

Bird[5] has claimed the preparation of the methyl, ethyl, phenyl and benzyl ethers by the reaction of organic halides with a solution of silver picrate in diethylene glycol monoethyl ether.

These reactions have been investigated. The method of Stenhouse and Muller[2] has been extended to cover the preparation of the methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl and isoamyl ethers. Attempts to prepare the *n*-amyl compound failed. The method of Bird was found to yield picric acid in all the cases examined other than the preparation of ethyl picryl ether.

It has been found that silver picrate does not react with methyl, ethyl, *n*-propyl, *n*-butyl, *n*-amyl and isoamyl bromides when refluxed on the water-bath. The silver picrate was recovered unchanged.

The production of picric acid was observed in these reactions by Stenhouse and Muller.[2] This product is obtained in the presence of alcohol or benzene as solvents. The picric acid was shown not to result from hydrolysis by running the reactions under anhydrous conditions. When the reaction was carried out in a closed system and the gaseous products were swept through a solution of bromine in ligroin, the bromine was rapidly decolorized. That the alkyl radical was probably lost as the unsaturated hydrocarbon was shown in the case of *t*-butyl bromide by isolating 2-methyl-1,2-dibromopropane from the ligroin solution after decolorization. Silver picrate dehydrohalogenates the primary alkyl iodides examined above methyl at reflux temperatures. This reaction does not appear to have been reported and accounts for the production of picric acid frequently observed in these reactions. The three secondary iodides investigated gave picric acid at temperatures of 0° and higher. Isopropyl iodide gave the ether when the temperature was lowered to −60°. 2-Butyl and 3-pentyl iodides gave no reaction at −60°. *t*-Butyl bromide gave picric acid at all temperatures investigated (−60 to 72°).

In the course of this study two new alkyl picryl ethers, isopropyl picryl ether and *n*-butyl picryl ether, were prepared. The isopropyl compound appears to be the only picryl ether known with a secondary alkyl group. It has an unexpectedly high melting point and is resistant to hydrolysis in water or dilute hydrochloric acid.

The yields of the crude compound in these reactions varied from 30 to 80% based on silver picrate, and were somewhat variable. Practically all of the unreacted halide may be recovered and the yields based on halide are comparable if allowance is made for the recovered halide. The losses on recrystallization of the lower melting compounds are rather high. In most cases recrystallization is unnecessary.

Experimental[6]

Materials.—The alkyl halides used in this study were prepared by standard methods and dried over calcium chloride.

Bird's[5] directions for the preparation of silver picrate solutions call for the addition of the stoichiometric amount of picric acid to a suspension of "silver hydroxide" in diethylene glycol monoethyl ether, and heating the solution at 80° until the mixture gives a neutral reaction. We were unable to obtain neutral reactions from these solutions even with large excesses of "silver hydroxide." The following technique was employed in this study. "Silver hydroxide" was prepared by the slow addition of sodium hydroxide (24 g., 0.60 mole) dissolved in water (500 ml.) to silver nitrate (100 g., 0.56 mole) dissolved in water (500 ml.). The precipitated "silver hydroxide" was washed by decantation, filtered and transferred to a liter beaker containing diethylene glycol monoethyl ether (345 g., 350 ml.). Air dried picric acid (130 g., 0.56 mole) was added with stirring and the mixture was heated on an oil-bath at 90–95° for 45 minutes. The viscous solution was filtered with suction through an asbestos mat to remove a small quantity of unreacted "silver hydroxide." Dried "silver hydroxide" or commercial silver oxide with added water will not dissolve under these conditions.

Silver picrate[7] was prepared by diluting 300 ml. of the

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[1] Richmond Fellow 1949–1950. Part of this material is from a thesis submitted by D. J. Massey in partial fulfillment of the requirements for the degree of Master of Science in Chemistry.

[2] J. Stenhouse and H. Muller, *Ann.*, **141**, 80 (1867).

[3] A. F. Holleman, *Rec. trav. chim.*, **22**, 263 (1903).

[4] J. Meisenheimer, *Ann.*, **323**, 242 (1902).

[5] J. C. Bird and A. Barol, *J. Am. Pharm. Assoc.*, **23**, 996 (1934); J. C. Bird, U. S. Patent 2,165,111 (1937).

[6] All melting points are corrected. Other temperatures are uncorrected.

[7] Silver picrate is sensitive to heat and shock and has been employed as a detonator. The precautions appropriate to the preparation and handling of highly explosive compounds should be observed at all times.

silver picrate solution prepared above with twice its volume of water, chilling in an ice-bath until precipitation was complete, filtering with suction and washing with 50 ml. of ice-cold water. The precipitate was pressed as dry as possible with a rubber sheet then washed by decantation with three 200-ml. portions of dry thiophene-free benzene. It was then refiltered, washed on the filter with two 100-ml. portions of dry benzene and three 100-ml. portions of petroleum ether. The silver picrate was then dried *in vacuo* over calcium chloride. The silver content was determined by the method of metal residues and agreed with the theoretical within the limits of experimental error. This technique gives the anhydrous form of silver picrate. Bird[5] states that his procedure may give either the anhydrous or hydrated form.

Silver Picrate Solution with Alkyl Iodides.—Several alkyl iodides were investigated using Bird's technique. The following procedure was employed. Bird gives no specific directions.

Ethyl iodide (10 ml., 0.11 mole) was added to 40 ml. of the silver picrate solution prepared above. Precipitation of silver iodide occurred immediately and was complete in ten minutes. The solution was filtered from the silver iodide and the filtrate diluted with twice its volume of water. Fluffy light yellow needles of ethyl picryl ether precipitated. After one recrystallization from ethyl alcohol they melted at 78°.

The same procedure was repeated with methyl, *n*-propyl, isopropyl, 2-butyl, *t*-butyl and *n*-amyl iodides. In each of these cases silver iodide precipitated immediately. Dilution of the solution with water gave picric acid m.p. 121°: no depression when mixed with an authentic sample. Attempts were made to precipitate the ethers by the addition of solvents other than water. No precipitate was obtained in any case. Bromobenzene gave no reaction with silver picrate solution.

Silver Picrate with Alkyl Bromides.—No reference is made in the literature to the action of silver picrate on alkyl bromides.

Silver picrate (10 g., 0.03 mole) was added to ethyl bromide (20 ml., 0.22 mole) and the mixture was allowed to stand at room temperature for one hour. No reaction was apparent. The mixture was then refluxed for five minutes and filtered. No solid was obtained on evaporation of the excess alkyl bromide. The solid residue was shown to be unreacted silver picrate by reaction with methyl iodide to form methyl picryl ether. Refluxing for longer periods up to three hours did not change the results.

The above procedure was repeated with the same molar ratios using *n*-propyl, *n*-butyl, *n*-amyl and isoamyl bromides. There was no evidence of reaction in any case.

Silver Picrate and Primary Alkyl Iodides.—Silver picrate was treated with methyl, ethyl, *n*-propyl, *n*-butyl, isobutyl, *n*-amyl and isoamyl iodides. The *n*-propyl and isoamyl ethers have not been previously synthesized by this technique. The *n*-butyl ether has not been described. A typical experiment is described for *n*-butyl picryl ether. Data on the other reactions are given in Table I. In all cases the ether produced was recrystallized from the alcohol corresponding to the alkyl group present.

***n*-Butyl Picryl Ether.**—Silver picrate (10 g., 0.03 mole) was added to *n*-butyl iodide (30 ml., 0.26 mole) at 0° and allowed to stand at that temperature overnight. Silver iodide was removed by filtration and excess *n*-butyl iodide by vacuum distillation on a water-bath at 50°. The oily residue was dissolved in hot *n*-butyl alcohol. After standing for 3 days in the refrigerator at 5°, light yellow plates separated m.p. 36.5°; unchanged on recrystallization from *n*-butyl alcohol. Subsequent runs responded to seeding.

Anal. Calcd. for $C_{10}H_{11}N_3O_7$: C, 42.11; H, 3.88; N, 14.73. Found: C, 41.92; H, 3.95; N, 14.91.

When iodides higher than methyl reacted under reflux or in the presence of benzene or alcohol as solvents the principal product was picric acid.

Silver Picrate and Secondary Iodides.—Silver picrate was treated with isopropyl iodide, 2-butyl iodide and 3-pentyl iodide. The latter two compounds did not yield an ether. The preparation of the isopropyl ether is described. Data on the other reactions are given in Table I.

Preparation of Isopropyl Picryl Ether.—Isopropyl iodide (25 ml., 0.25 mole) was cooled to −60° in a Dry Ice–acetone-bath and silver picrate (10 g., 0.03 mole) was added slowly with stirring. The mixture was held at −60° for 5 hours then allowed to rise spontaneously to room temperature overnight. Silver iodide was removed by filtration and excess isopropyl iodide by vacuum evaporation. The residue was dissolved in hot isopropyl alcohol and cooled in the refrigerator. The light yellow plates (m.p. 95°) were washed with petroleum ether and dried. The melting point was unchanged by recrystallization from isopropyl alcohol. A mixed melting point with picric acid gave a depression of 25°. A mixed melting point with *n*-propyl picryl ether was depressed below room temperature.

TABLE I

Alkyl-I	Temp., °C.	Time, hours	Product	M.p., °C. Found	M.p., °C. Reported
Methyl	0	3	Ether	68	68[a]
Ethyl	0	3	Ether	78	78[b]
n-Propyl	0	3	Ether	38	43[c]
n-Butyl	0	15	Ether	36.5	..
Isobutyl	0	15	Ether	55	55[d]
n-Amyl	0	15	Oil[e]	...	..
Isoamyl	0	15	Ether	56	69[f]
Isopropyl	0	*g*	Picric acid	121	121
Isopropyl	−60	5	Ether	95	..
2-Butyl	0	*h*	Picric acid	121	121
3-Pentyl	0	*h*	Picric acid	121	121
t-Butyl-Br	−60	*g*	Picric acid	121	121

[a] A. Cahours, *Ann. chim. phys.*, [3] **25**, 25 (1849). [b] A. Cahours, *ibid.*, [3] **27**, 441 (1849). [c] C. L. Jackson and W. R. Boos, THIS JOURNAL, **20**, 444 (1898). Discrepancy may be due to polymorphism. *Anal.* Calcd. for $C_9H_9N_3O_7$: C, 39.85; H, 3.32; N, 15.49. Found: C, 39.94; H, 3.41; N, 15.53. [d] Meisenheimer, ref. 4. [e] The product was a viscous oil which deposited some picric acid after standing for two weeks *in vacuo* over sulfuric acid and paraffin shavings. [f] Jackson and Boos, *loc. cit.* *Anal.* Calcd. for $C_{11}H_{13}N_3O_7$: C, 44.15; H, 4.35; N, 14.04. Found: C, 44.26; H, 4.22; N, 14.11. [g] Immediate reaction with the separation of silver iodide. [h] Immediate reaction with the separation of silver iodide. No reaction at −60°.

Anal. Calcd. for $C_9H_9N_3O_7$: C, 39.85; H, 3.32; N, 15.49. Found: C, 39.74; H, 3.19; N, 15.71.

Samples of isopropyl picryl ether were recovered unchanged after boiling with water or aqueous 1% hydrochloric acid for one hour.

Silver Picrate and *t*-Butyl Bromide.—When silver picrate was treated with *t*-butyl bromide an immediate reaction occurred at all temperatures from room temperature down to −60° with picric acid as the only solid product isolated.

Dehydrohalogenation.—A two-neck flask was equipped with a reflux condenser the top of which was connected to a gas absorber. A stream of nitrogen was passed into the apparatus through the second neck. The apparatus was thoroughly dried and swept with nitrogen. The absorber was filled with a solution of bromine (0.6 g.) in ligroin (b.p. 60–90°, 30 ml.). Silver picrate (10 g., 0.03 mole) and *t*-butyl bromide (10 ml., 0.09 mole) were introduced and the mixture was heated to reflux on a water-bath. A slow stream of nitrogen was passed through the apparatus. The bromine solution was decolorized in 20 minutes. The ligroin was evaporated on a water-bath and the liquid residue was distilled (b.p. 150°) in a semi-micro fractionating column; reported for 2-methyl-1,2-dibromopropane, 149–151°.[8]

Isopropyl iodide under the same conditions gave a gaseous product which decolorized bromine and reduced potassium permanganate. No attempt was made to isolate the dibromide.

In blank runs with no silver picrate the bromine was not decolorized in either case.

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(8) W. Krestinsky, *Ber.*, **55**, 2757 (1922).