The Propyl, Allyl and Propargyl Ethers of Picric Acid[1]

BY A. H. BLATT AND A. W. RYTINA[2]

We were unable to find satisfactory procedures in the literature for preparing picryl alkyl ethers and it was therefore necessary to modify existing procedures in order to make the propyl, allyl and propargyl ethers of picric acid. The directions of Fairbourne and Foster[3] for preparing picryl allyl ether—which call for the addition of a solution of one mole of picryl chloride in allyl alcohol to a solution of one mole of potassium hydroxide in the same solvent, and which have the disadvantage of giving erratic results—were selected as being most readily adapted to our needs. By the use of slightly more than two moles of potassium hydroxide per mole of picryl chloride, by suitable control of the reaction temperature and time, and by selection of the proper conditions for isolating the products, consistently satisfactory results were obtained. The ethers are present in the reaction mixture as sodium hydroxide or sodium alkoxide addition products and the base must be removed in such a way as to minimize the hydrolysis of the ethers. Because the addition products differ in stability and the ethers differ in ease of hydrolysis, it is necessary to specify the conditions for the isolation of each ether and it is necessary to adhere closely to the conditions specified. For the same reasons it is not possible to give a generalized procedure for the preparation of other picryl alkyl ethers.

Picryl propyl ether[4] and picryl allyl ether[3,5] have been described earlier. Picryl propargyl ether is a new compound. Attempts to prepare it from the dibromide of picryl allyl ether[3,5] were not successful; treatment of the dibromide with pyridine resulted in cleavage with the formation of pyridine picrate, potassium hydroxide in ethyl alcohol brought about alcohol interchange to yield the ethyl ether, and potassium hydroxide in *t*-butyl alcohol was without action. The three ethers are high explosives. Their performance in the lead block as determined by Mr. Harold Gammel and expressed as percentages of the performance of TNT is: picryl propyl ether, 68%; picryl allyl ether, 85%; picryl propargyl ether, 99%. The effect of unsaturation upon the power of these explosives is to be noted.

Experimental

Preparation of Picryl Propyl Ether.—A warm solution of 4.9 g. (0.02 mole) of picryl chloride in 55 ml. of *n*-propyl alcohol was added to an ice-cold solution of 2.3 g. (0.041 mole) of potassium hydroxide in 60 ml. of *n*-propyl alcohol. The reaction mixture turned bright red and an orange precipitate began to form almost immediately. After a half-hour the reaction mixture was removed from the ice-bath and left for twenty hours. The precipitate was filtered and washed with 25 ml. of ice-cold *n*-propyl alcohol. It was then suspended in 300 ml. of cold water and stirred in order to break up lumps. Five milliliters of 10% hydrochloric acid was added and stirring was continued for five minutes. The yellow solid was filtered and stirred with water and hydrochloric acid as before to complete the decomposition of the few remaining flecks of orange solid. Finally the precipitate was filtered and washed with cold water until the washings were colorless. The products from five such runs were combined and dried in a vacuum desiccator to yield 19 g. (70%) of crude product. The solid was dissolved in 75 ml. of anhydrous ether, warmed with decolorizing carbon, filtered, concentrated to 50 ml., and diluted with ligroin. On chilling, 16.5 g. of pure product melting at 39.5–40° was obtained; yield 61%.

Preparation of Picryl Allyl Ether.—A solution of 4.9 g. (0.02 mole) of picryl chloride in 30 ml. of allyl alcohol was added to an ice-cold solution of 2.3 g. (0.041 mole) of potassium hydroxide in 20 ml. of allyl alcohol. After an hour at the temperature of the ice-bath and twenty hours at room temperature, the reaction mixture was poured into 250 ml. of water containing 20 drops of glacial acetic acid. The aqueous solution and suspended solid were stirred for five minutes, then the solid was separated by filtration and washed with cold water until the washings were colorless. The combined products from three such runs after drying in a desiccator weighed 6.0 g.; 38% yield. The crude ether was dissolved in 20 ml. of benzene, the solution was treated with decolorizing carbon and diluted with 20 ml. of ligroin. The yield of the pure ether, an almost colorless solid melting at 85–86°, was 5.1 g. or 32%.

Preparation of Picryl Propargyl Ether.—A solution of 4.0 g. (0.016 mole) of picryl chloride in 15 ml. of propargyl alcohol was added to an ice-cold solution of 2.0 g. (0.036 mole) of potassium hydroxide in 12 ml. of propargyl alcohol. The reaction mixture was kept in an ice-bath for one-half hour, left at room temperature for eighteen hours, and poured with stirring into 450 ml. of cold water containing 20 drops of glacial acetic acid. The precipitate was filtered, suspended in 300 ml. of water containing ten drops of dilute hydrochloric acid, and stirred until the red color of the solid disappeared. The yellow solid was then washed with cold water until the washings were colorless. The products from ten such runs were combined and dried in a vacuum desiccator to yield 25.8 g. of crude product; 60% yield. The solid was crystallized first from 1 l. of anhydrous ether with the use of decolorizing carbon, and then from a mixture of 100 ml. of toluene and an equal volume of ligroin. The yield of pure product, light yellow needles melting at 99–100°, was 21.0 g. or 49%.

Anal. Calcd. for $C_9H_5N_3O_7$: C, 40.45; H, 1.87; N, 15.73. Found: C, 40.29; H, 2.29; N, 16.4.

The propargyl ether in chloroform solution treated with three moles of bromine in the same solvent furnishes in 87% yield a dibromide which crystallizes from anhydrous ether in long white needles melting at 96.5–97.5°.

Anal. Calcd. for $C_9H_5N_3O_7Br_2$: Br, 38.17. Found: Br, 38.01, 38.27.

FLUSHING, L. I., N. Y. RECEIVED JANUARY 19, 1950

---

[1] This note is based on work done under Contract W-19-020-ORD-6436 with the Office of the Chief of Ordnance and has been approved for publication by the Public Information Division, National Military Establishment.

[2] Rohm & Haas Co., Philadelphia, Pennsylvania.

[3] Fairbourne and Foster, *J. Chem. Soc.*, 3148 (1926).

[4] Jackson and Boos, *Am. Chem. J.*, **20**, 444 (1898).

[5] Raiford and Birosle, THIS JOURNAL, **51**, 1778 (1929).

Allopregnan-3β-yl Acetate

BY D. H. R. BARTON[1] AND N. J. HOLNESS

Recently Huang-Minlon[2] reported the preparation, by the modified Wolff-Kishner reduction of allopregnan-3β-ol-20-one, of allopregnan-3β-ol, m. p. 136–137°, $[\alpha]_D$ +18° (in chloroform). The

---

[1] Harvard University Visiting Lecturer, 1949–1950.

[2] Huang-Minlon, THIS JOURNAL, **71**, 3301 (1949).