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.

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(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).

physical constants were in good agreement with those recorded previously.[3] Acetylation gave the corresponding acetate, m. p. 115–116°,[5] for which the specific rotation of −61° (in chloroform) was claimed. According to standard tables[6] allopregnan-3β-ol and its acetate would be expected to have specific rotations of +16 and +6°, respectively. Since Huang-Minlon's recorded rotation of −61° was so different from the expected value and since these are compounds in which "vicinal action" would not be anticipated[7] to invalidate the comparison of molecular rotations, it seemed to us to be worthwhile to reinvestigate the properties of allopregnan-3β-ol and its derivatives. For the acetate of allopregnan-3β-ol we now find, m. p. 113–114°, $[\alpha]_D$ +5° (in chloroform).[8] A summary of the molecular rotations of allopregnan-3β-ol derivatives given in the Table shows that the values are in excellent agreement with those found in the cholestane series. The replacement of the saturated isoöctyl side chain of cholestanol by an ethyl group causes no "vicinal action" at the 3-position.

TABLE I

Substance	$[M]_D$ (in chloroform) Alcohol	Acetate	Benzoate	Ketone	Δ_1[a]	Δ_2	Δ_3
Cholestan-3β-ol[b]	+ 89	+ 60	+ 94	+162	−29	+5	+73
Allopregnan-3β-ol	+ 48	+ 17	+ 49	+120	−31	+1	+72
Δ⁵-Pregnen-3β-ol[c]	−181	−214	−105	+331			
Δ[d]	+229	+231	+154	−211			
Compare standard Δ values[e]	+243	+248	+168	−195			

[a] Δ_1 is the increment in molecular rotation on acetylation, Δ_2 that on benzoylation and Δ_3 that on oxidation to the ketone. [b] Barton, *J. Chem. Soc.*, 1116 (1946). [c] Barton, Holness and Klyne, *ibid.*, 2456 (1949). [d] Difference in molecular rotation on saturation of the Δ⁵-ethylenic linkage. [e] From the cholesterol-cholestanol series; see Barton and Cox, *ibid.*, 783 (1948).

Experimental[9]

The standard chemical operations of acetylation, benzoylation, alkaline hydrolysis, etc., were carried out as detailed previously.[10]

Allopregnan-3β-yl Acetate.—This compound was prepared by the hydrogenation of Δ⁵-pregnen-3β-yl acetate (from 600 mg. of Δ⁵-pregnen-3β-ol-20-one acetate)[11] in 25 ml. of acetic acid at room temperature using 100 mg. of platinum oxide catalyst. After working up in the usual manner the product was chromatographed over alumina (Savory and Moore's standardized) to give six fractions m. p.'s 105–110°, 107–111°, 110–112°, 109–111°, 111–113° and 110–113°. The last five were recrystallized three times from chloroform–methanol to give 405 mg. of pure allopregnan-3β-yl acetate, m. p. 113–114°, $[\alpha]_D$ + 5° (*c*, 2.28), + 6° (*c*, 1.40).

Allopregnan-3β-ol and Derivatives.—Alkaline hydrolysis of allopregnan-3β-yl acetate afforded allopregnan-3β-ol, recrystallized from methanol, m. p. 135–137°, $[\alpha]_D$ + 16° (*c*, 3.15). Benzoylation of the latter furnished allopregnan-3β-yl benzoate, recrystallized from chloroform–methanol, m. p. 154–155°, $[\alpha]_D$ + 12° (*c*, 1.67).

Anal. Calcd. for $C_{28}H_{40}O_2$: C, 82.28; H, 9.91. Found: C, 82.25; H, 9.8.

Chromic acid oxidation of allopregnan-3β-ol and chromatography over alumina (Savory and Moore's standardized) gave allopregnan-3-one, recrystallized from methanol, m. p. 112–113°, $[\alpha]_D$ + 39° (*c*, 0.91).[12]

(3) (a) Ruzicka, Meister and Prelog[4a] gave m. p. 137–138°, $[\alpha]_D$ +18°. (b) Ruzicka, Goldberg and Hardegger[4b] found m. p. 137–138°, $[\alpha]_D$ +16°. Both rotations in chloroform.

(4) (a) Ruzicka, Meister and Prelog, *Helv. Chim. Acta*, **30**, 867 (1947); (b) **22**, 1294 (1939).

(5) Ruzicka, Goldberg and Hardegger[4b] found m. p. 115–116°. The rotation was not recorded.

(6) Barton and Klyne, *Chem. and Ind.*, 755 (1948).

(7) Barton and Cox, *Nature*, **159**, 470 (1947); *J. Chem. Soc.*, 783 (1948); Barton, *Angew. Chem.*, **61**, 57 (1949).

(8) The m. p. is in agreement with previous workers[2,5] and there seems no reason to doubt the purity of Huang-Minlon's preparation.

(9) M. p.'s are not corrected. All specimens were dried *in vacuo* at 20° below their m. p.'s or at 120°, whichever was the lower temperature, before taking the rotation. All rotations are for the sodium D line and in chloroform solution. The measurements were made at room temperature which varied from 15 to 25°. All values of $[\alpha]_D$ have been approximated to the nearest degree. Concentrations (*c*) are expressed in g. per 100 ml.

(10) Barton and Cox, *J. Chem. Soc.*, 783 (1948).

(11) Barton, Holness and Klyne, *ibid.*, 2456 (1949).

(12) Ruzicka, Meister and Prelog[4a] found m. p. 116–118°, $[\alpha]_D$ +44° (in chloroform). Ruzicka, Goldberg and Hardegger[4b] gave m. p. 116–117°.

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Olefins from Alcohols

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The conversion of alcohols into olefins, one of the fundamental operations in organic chemistry, can be accomplished by several well-known methods. However, the dehydration of primary alcohols is invariably difficult except in the case of the low-molecular aliphatic alcohols. No general method is known which would accomplish this conversion in good yield.

We wish to record a new method for the preparation of olefins from alcohols which effects this conversion in excellent yields by the use of a mild catalyst and is applicable to primary alcohols, as well as secondary and tertiary. We have found that the dehydration of alcohols can be effected almost quantitatively by the use of boric acid or anhydride as catalyst. The study of the mechanism of this reaction showed that it involves two steps: (1) the formation of the boric ester and (2) the decomposition of the boric ester into the olefin with the regeneration of the catalyst

$$3R{-}CH_2CH_2OH + H_3BO_3 \longrightarrow B(OCH_2CH_2R)_3 \longrightarrow 3R{-}CH{=}CH_2 + H_3BO_3$$

The new method is thus similar to the one involving the pyrolysis of acetates[1] except that the reaction proceeds at much lower temperatures and is of a true catalytic character. However, a comparison of the two methods is not possible at this time since the pyrolysis of the acetates has been applied only to a few rather special cases

(1) Frank, Berry and Shotwell, THIS JOURNAL, **71**, 3889 (1949); Burns, Jones and Richie, *J. Chem. Soc.*, 400 (1935); Schniepp and Geller, THIS JOURNAL, **67**, 54 (1945); Ratchford and Fisher, *ibid.*, **69**, 1911 (1947).