NOTES

Ribitol Pentaacetate

By W. W. Binkley[1] and M. L. Wolfrom

The acetates of the sugars and sugar alcohols are significant reference compounds especially in certain types of chromatographic techniques.[2] All of the acetates of the pentitols have been described in crystalline form save that of ribitol (synonym, adonitol). We wish to report herein the crystallization of such a derivative of this naturally occurring pentitol.

Experimental

A mixture of 2.00 g. of ribitol, 0.3 to 0.4 g. of freshly fused zinc chloride, and 20 ml. of acetic anhydride was surrounded with an ice- and water-bath and was stirred for sixteen hours. The temperature of the bath was allowed to rise gradually to 25° during this period. The reaction mixture was poured on 30 g. of finely crushed ice, was stirred for thirty minutes, and was adjusted to a *p*H of 6 with sodium bicarbonate. This solution was extracted with four 25-ml. portions of chloroform. Solvent removal from the dried extract yielded crystalline material; yield 4.78 g. Pure material was obtained on recrystallization from diethyl ether; yield 3.87 g., m. p. 51°. A further crop of less pure material (0.33 g.) was obtainable from the mother liquor on the addition of petroleum ether (b. p. 60–65°). The substance crystallized in elongated prisms that were soluble in benzene, chloroform, ethanol and diethyl ether.

Anal. Calcd. for $C_{15}H_{22}O_{10}$: C, 49.72; H, 6.12; CH_3CO, 13.80 ml. of 0.1 *N* NaOH per 100 mg. Found: C, 49.62; H, 6.07; CH_3CO, 13.82 ml.

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[1] Sugar Research Foundation Fellow of The Ohio State University Research Foundation (Project 190).

[2] W. H. McNeely, W. W. Binkley and M. L. Wolfrom, This Journal, **67**, 527 (1945).

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Dihydro-*exo*-dicyclopentadiene

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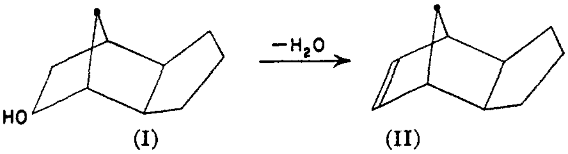
Recently Bartlett and Goldstein[2] showed that the hitherto rare *exo* isomer of dicyclopentadiene can be readily obtained by dehydrohalogenation of iodo-dihydro-*exo*-dicyclopentadiene[3] which may conveniently be prepared by warming ordinary *endo*-dicyclopentadiene with hydriodic acid.[3]

By dehydrating hydroxy-tetrahydro-*exo*-dicyclopentadiene[4] (I) with phosphoric acid we have obtained the corresponding dihydro-*exo*-dicyclopentadiene (II) in which the residual double bond is in the bridge endomethylene ring.



(I) (II)

This completes the series of isomeric dihydrodicyclopentadienes.

Experimental

Dihydro-*exo*-dicyclopentadiene.—A mixture of 15 g. of sirupy 85% phosphoric acid and 198 g. of hydroxy-tetrahydro-*exo*-dicyclopentadiene[4] which had twice been recrystallized from nitroethane to m. p. 53°, was stirred and heated in an oil-bath under a reflux condenser to which was attached a water separator device. After heating for about one hour at 150–230°, 40 cc. of oily liquid and 20 cc. of water had collected in the separator. The residual oil in the still flask was washed with water and distilled under reduced pressure to yield 40 g. of oil boiling at 80–95° (40 mm.). This was combined with the 40 cc. of oil distillate and the mixture redistilled. A fraction (68 g.) boiling at 89–93° (40 mm.) was thus secured. This was refractionated through an efficient packed column to yield 61 g. of colorless oil b. p. 89–91° (39 mm.) having n^{25}_D 1.4993; d^{25}_4 0.9571. It boiled at 182° (768 mm.).

Anal. Calcd. for $C_{10}H_{14}$: C, 89.55; H, 10.44. Found: C, 89.45; H, 10.43.

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[1] Present address: Industrial Rayon Corporation, Cleveland, Ohio.

[2] Bartlett and Goldstein, This Journal, **69**, 2553 (1947).

[3] Previously referred to as iodo-dihydro-*nor*-dicyclopentadiene, Bruson and Riener, *ibid.*, **67**, 1179 (1945).

[4] Previously referred to as hydroxy-tetrahydro-*nor*-dicyclopentadiene, Bruson and Riener, *ibid.*, **67**, 727 (1945).

Addition of Organolithium Compounds to the Azomethine Linkage of γ-Picoline and 6-Methoxyquinoline

By Henry Gilman and H. Smith Broadbent[1]

In connection with some studies on compounds having possible physiological activity, occasion arose to prepare some "anil addition" compounds of γ-picoline and 6-methoxyquinoline.

At −80° *n*-butyllithium was found to be without observable action on γ-picoline in ether solution. Upon carbonation of the reaction mixture, γ-picoline and valeric acid were the only isolable products. At −10°, however, addition to the anil linkage is the predominant reaction yielding first the lithium salt of 2-*n*-butyl-4-methyl-1,2-dihydropyridine (not isolated) which upon acidification and air oxidation gave 2-*n*-butyl-4-methylpyridine.

Addition of α-thienyllithium to 6-methoxyquinoline at the reflux temperature of ether similarly yielded 2-(α-thienyl)-6-methoxyquinoline.

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