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Note

Trace analysis of 1,2-ethanediol by gas-liquid chromatography of its cyclic *n*-butylboronate

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Because of its high polarity and low volatility, 1,2-ethanediol, when subjected to direct gas chromatographic analysis, exhibits the adsorption and subsequent desorption phenomena referred to as "memory effects" or as "ghosting"¹⁻⁴. It was considered that available means¹⁻⁴ of overcoming this problem were not suited for the development of a routine method designed for use either by relatively unskilled personnel or in the presence of large excesses of other materials (e.g. steroids). Derivatisation of the hydroxyl groups was therefore appropriate but the obvious choice of silylation^{5,6} proved to be inadequate. Results obtained with a wide range of silylating agents and columns under various conditions showed that peaks corresponding to the derivatives formed were poorly resolved from excess reagent or from reagent impurities. The potential for loss of the volatile derivatives precluded removal of excess reagent.

This note describes a convenient analysis of trace quantities of 1,2-ethanediol as 2-*n*-butyl-1,3,2-dioxaborolane. The use of cyclic boronates in gas chromatography was introduced by Brooks and Watson⁷ and is now well established⁸⁻¹⁰. However, despite reports indicating formation of the cyclic *n*-butylboronates of 1,2-ethanediol¹¹ and 1,3-propanediol⁷⁻¹⁰, the derivatives do not appear to have been used for analytical purposes.

EXPERIMENTAL

Materials

Acetone was analytical reagent grade, 1,2-ethanediol and 1,3-propanediol (internal standard) were laboratory reagents. *n*-Butylboronic acid (Applied Science Labs., State College, Pa., U.S.A.), when not in use was stored tightly stoppered at 0°.

A Pye 104 gas chromatograph, equipped with a flame ionisation detector and heated injection port was used. Chromatography was performed at 100° using a 2 m × 4 mm I.D. glass column packed with 20% OV-17 on Gas-Chrom Q, (100-120 mesh) with nitrogen (60 ml/min) carrier gas. The column was deactivated with Silyl-8 (Pierce, Rockford, Ill., U.S.A.) before use.

Electron impact (EI) mass spectra were obtained (by Mr. M. T. Davies of this Company) on a Varian-MAT 311A double focussing mass spectrometer following separation in a modified Varian 2740 gas chromatograph.

Derivative formation

1,2-Ethanediol was found to react smoothly with *n*-butylboronic acid in acetone at ambient temperature, producing the anticipated derivative (confirmed by EI mass spectrometry). 2-*n*-Butyl-1,3,2-dioxaborolane showed excellent chromatographic properties, having a retention, relative to 1,3-propanediol cyclic *n*-butylboronate (2-*n*-butyl-1,3,2-dioxaborinane) (*ca.* 20 min), of 0.47. Resolution from the acetone tail was adequate. The formation of the cyclic boronates was followed and appeared to be complete after 20 min, the products remaining stable for at least 3 days when kept at 0° or 6 h at ambient temperature. Completion of the reaction rather than attainment of equilibrium was indicated by the fact that the yield was not significantly affected either by addition of excess water (up to 10%, v/v) or by incorporation of a water scavenger (2,2-dimethoxypropane) into the reaction mixture. In the absence of pure samples of the derivatives (which would facilitate stoichiometric assessment of the extent of the reaction) a minimum reaction time of half an hour was selected.

Procedure

Reference standard solutions were obtained by serial dilution (with acetone) of a 2.0% (v/v) acetone solution of 1,2-ethanediol. 1,3-Propanediol (final concentration 0.01%, v/v) and *n*-butylboronic acid (final concentration 2.0%, w/v) were added at time $t = 0$ and reaction was allowed to proceed until time $t = 30$ min. Aliquots (1 μ l) of the reaction mixture were then injected into the heated (175°) injection port. Sample solutions, containing concentrations of internal standard and reagent identical with those in the reference standard solutions, were treated similarly, enabling unknown 1,2-ethanediol concentrations to be estimated by reference to the appropriate reference standard. After 8–10 injections, the column temperature was temporarily raised to 200° whilst the peaks due to tri-*n*-butylboroxin (formed by condensation and cyclisation of three reagent molecules) were eluted.

RESULTS AND DISCUSSION

Calibration graphs, passing through the origin, were linear in the 1,2-ethanediol concentration range 0.001%–0.4% (v/v). The detection limit was generally found to be around 0.0003% (3 ppm). The formation of the cyclic *n*-butylboronate, apart from facilitating chromatography of low levels of 1,2-ethanediol, is advantageous for two other reasons: (i) it confers a considerable degree of selectivity to the method (since other cyclic boronates elute later) and (ii) it markedly increases the effective molar response of 1,2-ethanediol in the flame ionisation detector.

This procedure constitutes a convenient alternative to other means of determining trace amounts of 1,2-ethanediol. There is no reason why the method should not be extended to the estimation of larger quantities of the diol and to the determination of the propanediols. It should be possible to analyse even smaller amounts of 1,2-ethanediol by adapting this procedure so as to enable the use of cyclic butylboronates possessing electron capturing properties, such as those recently reported by Poole *et al.*^{12,13}.

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