Preparation and Identification of 2-Chloroethyl 1-Naphthyl Acetate

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In the past few years, increased interest in the physiological properties of naphthaleneacetic acid and its derivatives has been apparent. Guthrie (1) described the use of the methyl ester of naphthaleneacetic acid to inhibit the growth of potato tubers and to induce epinasty of tomato leaves. Mitchell and Stewart (2) studied the use of naphthaleneacetic acid to induce growth response in plants. Hesse and Davey (3, 4) experimented with naphthaleneacetic acid in the control of fruit drop of pear, apricot, and peach trees. Hartmann (5) employed naphthaleneacetic acid in a spray for thinning in olive trees to increase fruit size and provide for a normal crop set the following year.

Since naphthaleneacetic acid has been so widely used in agriculture, it has become increasingly important to have a sensitive analytical procedure for detecting it in fruits and leaves. Coulson et al. (6) have described a method based on gas chromatography and microcoulometric detection for chlorinated organic pesticides. Goodwin et al. (7) have detected chlorinated organic compounds by gas chromatography and electron affinity detection. Since these methods have an advantage of being extremely sensitive and have an increased specificity due to the halogen in the molecule, the analysis of 1-naphthaleneacetic acid as its chloro-ester

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was undertaken. Success has been achieved in preliminary evaluation of the residue analysis for naphthaleneacetic acid as 2-chloroethyl 1-naphthyl acetate by gas chromatography in combination with the microcoulometric or electron affinity detectors.

The synthesis and identification of 2-chloroethyl 1-naphthyl acetate as a primary standard for analysis by gas chromatography is described below.

Experimental

Chemicals and Equipment. The 2-chloroethyl esters of short chain fatty acids have been prepared by Oette and Ahrens (8) for quantitative determination by gas-liquid chromatography. The preparation of 2-chloroethyl 1-naphthyl acetate was undertaken using this method with the following modifications:

Five grams of recrystallized α-Naphthaleneacetic acid (m.p. 130.5-131.5°C) was dissolved in 15 ml of redistilled 2-chloroethanol (b.p. 128.0-128.8°C) containing 10% (w/w) of boron trifluoride as described by Metcalfe and Schmitz (9). The solution was sealed in a 16 x 20 mm. Pyrex tube and heated for 20 minutes in a boiling water bath. The mixture was cooled in an ice bath and transferred to a 250 ml separatory funnel with three rinses of 33 ml of distilled water and several small rinses of petroleum ether. The water layer was extracted with three 100 ml portions of petroleum ether. The pooled petroleum ether extract was washed with 100 ml of distilled water, dried over anhydrous sodium sulfate, quantitatively filtered, and evaporated free of solvent under a warm air stream. The crude yield of ester was 93.7%.

Results and Discussion

The ester was purified by vacuum distillation to provide a clear, straw-colored liquid, b.p. 167°C (2.5 mm.), N^{20} D 1.5922.

Anal. Calcd. for $C_{14}H_{13}O_2Cl$: C, 67.59; H, 5.27; Cl, 14.26. Found: C, 67.68; H, 5.28; Cl, 14.12.

The infrared and ultraviolet spectra were consistent with the proposed structure.

2-Chloroethyl 1-naphthyl acetate analyzed by gas chromatography and microcoulometry gave a single peak with a retention time of 2.7 minutes at 245°C and 100 ml per minute of nitrogen carrier gas. A 6-foot 1/4-inch O.D. stainless steel column was packed with 30/60 mesh acid washed Chromosorb R coated with 20% Dow 11 silicone grease.

2-Chloroethyl 1-naphthyl acetate analyzed by gas chromatography and electron affinity detector gave a single peak with a retention time of 3.5 minutes at 200°C and 80 ml per minute of nitrogen carrier gas. An 8-foot 1/8-inch O.D. stainless steel column was packed with 60/80 mesh Chromosorb W (HMDS) coated with a mixture of 5% Dow 710 silicone fluid and 5% SE-30 gum rubber.

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