in the capillary withdrawal tube on the absorption flask was not included. This factor was included in Howland's calculations since the capillary withdrawal tube contained some hydrogen bromide gas which was pushed over with the sample into the sample flask. It can, however, be justifiably omitted from our calculations since the first few milliliters of sample and any hydrogen bromide gas in the tube were collected in a trap and did not enter the sample flask.

$$K_s = \frac{N_{HBr}}{P_{HBr}}$$

$$N_{HBr} = \frac{\frac{ml \times N}{1000}}{\frac{\text{wt of sample} - b}{\text{mol wt of solvent}} + \frac{ml \times N}{1000}}$$

$$P_{HBr} = P_{total} - P_{solvent}(1 - N_{HBr})$$

where N_{HBr} = mole fraction of HBr in each sample, P_{HBr} = partial pressure of HBr in the gas phase, K_s = solubility constant, ml = milliliters of NaOH solution used for titration, N = normality of NaOH, b = weight in grams of gas in sample, P_{total} = total pressure in millimeters, $P_{solvent}$ = vapor pressure of pure solvent in millimeters.

Registry No.—Hydrogen bromide, 10035-10-6; deuterium bromide, 13536-59-9.

Direct Synthesis of 1,1,4,4-Tetraethylpiperazinium Dichloride

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The formation of 1,1,4,4-tetraethylpiperazinium dichloride has been reported[2-6] on a number of occasions where the hydrochloride of β-chloroethyldiethylamine was treated in alkaline media. The unstable chloroamine cyclodimerizes to the title product through the aziridine intermediate.[5] Cope[7] has reported formation of the tetraalkylpiperazinium salts under acidic conditions. We wish to report a facile single-step process which gives practically quantitative yields of the tetraalkylpiperazinium dichloride when β-chloroethyldiethylamine hydrochloride is added to an epoxide, which acts as an acid scavenger and is converted into the chlorohydrin.

Experimental Section

To 17.0 g (0.099 mole) of β-chloroethyldiethylamine hydrochloride, reagent grade recrystallized from absolute ethanol, in 50 ml of absolute ethanol was added 10 g (0.108 mole) of 1,2-epoxy-3-chloropropane (epichlorohydrin). The mixture became homogeneous when heated to approximately 60°. Crystals of the product formed within 30 min; the reaction mixture was maintained at 60° for an additional 1.5 hr and then cooled to −10° to give 13.3 g (97%) of white crystalline product (dec. 270°). The presence of 1,3-dichloropropanol in the alcoholic mother liquor was shown by glpc. The DTA curve showed an initial rapid endotherm at 270° which continued to 342°. The infrared spectrum contained no peaks due to unsaturation or NH^+.

Anal. Calcd for $C_6H_{14}NCl$: C, 53.14; N, 10.33; H, 10.33; total Cl, 26.20; ionic Cl, 26.20. Found: C, 53.13; N, 10.33; H, 10.32; total Cl, 26.25; ionic Cl, 25.91.

The reaction can be run neat, using epichlorohydrin as the solvent and the acid scavenger, to give a 95% yield. Epoxides other than epichlorohydrin can be used. For example, 1,2-epoxybutane at a 1:1 mole ratio in absolute ethanol gave a 95% yield of the piperazinium dichloride product.

Registry No.—1,1,4,4-Tetraethylpiperazinium dichloride, 5449-19-4.

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Preparation of 2-Carbethoxycyclopentane-1,3-dione

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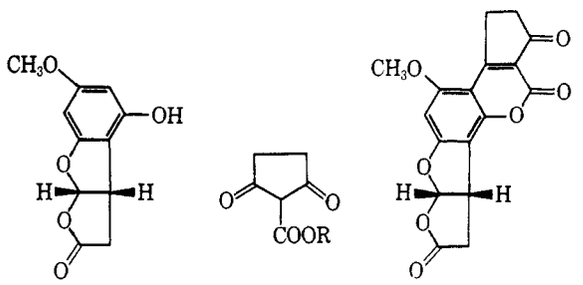
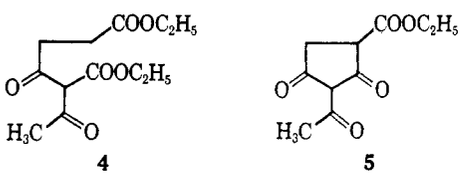
Condensation of phenol **1** with a 2-carbalkoxycyclopentane-1,3-dione (**2**) appeared to be an expeditious method for the preparation of the pentacyclic coumarin **3** which is an intermediate in the synthesis of aflatoxin B_1.[2] Syntheses of 2-carbethoxycyclopentane-1,3-dione (**12**) have been claimed in the literature but none could be verified.[3] The most direct approach



1 2 3

involving a Dieckmann cyclization of methyl ethyl β-ketoadipate could never be reduced to practice[3] but the successful cyclization of 1,4-dicarbethoxyhexane-3,5-dione (**4**) to 2-acetyl-4-carbethoxycyclopentane-1,3-dione (**5**)[4] led us to investigate the cyclization of



4 5

the corresponding malonic ester **6**. This intermediate has now been synthesized as follows.

The mixed anhydride prepared from ethyl chloroformate and *t*-butyl hydrogen succinate in the presence of triethylamine was condensed with diethyl ethoxymagnesiomalonate to give diethyl 3-carbo-*t*-butoxy-

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