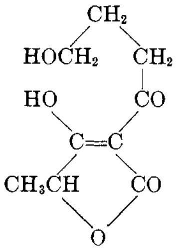
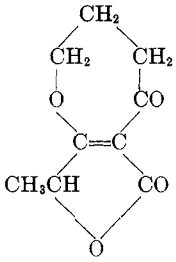


I



II

due to a proton in a hydrogen-bonded hydroxyl group ($\delta \sim 13$ p.p.m.). An integrated spectrum shows the presence of ten proton signals which occur in the following regions: (a) $\delta = 1.45$ p.p.m., a doublet (3 protons) due to the methyl group coupled with a single hydrogen atom $CH_3\text{-}\overset{|}{\underset{|}{C}}\text{-}H$; (b) $\delta = 2.35$ p.p.m., a multiplet (5 lines, 2 protons) due to the protons of the central methylene group of the seven-membered ring coupled with their neighbours; (c) $\delta = 3.45$ p.p.m., a triplet (2 protons) probably due to the hydrogen atoms of the $-CH_2CO$ group (this allocation is based on a study of other α-acyl tetronic acids[5]); (d) $\delta = 4.63$ p.p.m., a quartet ascribed to the single hydrogen atom of the $CH_3\overset{|}{\underset{|}{C}}\text{-}H$ group coupled with the protons of the methyl group; (e) $\delta = 4.82$ p.p.m., a triplet probably due to the two remaining methylene protons which are linked to oxygen in the group $-OCH_2CH_2CH_2CO-$. Integration of signals d and e shows the presence of three protons.

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A New Method for Preparing Ethyl Peroxide ("Diethyl Peroxide")

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An important member of the dialkyl peroxide series, ethyl peroxide, has been difficult to prepare in good yield until rather recently. First synthesized by Baeyer and Villiger[2] in 1900, no yields greater than 5% were reported until 1944, when Du Pont[3] disclosed that improved yields could be obtained by the repetitive addition of hydrogen peroxide to a heated mixture of diethyl sulfate and aqueous potassium hydroxide, with the ethyl peroxide distilling as formed. However, the yield of purified peroxide is only moderate, and the operation is extremely hazardous. Recently, Nangia and Benson[4] described an improved yield of about 30% by the use of sodium stearate as dispersing agent. In all of these cases, ethyl sulfate was used as the reactant.

In the course of preparing ethyl peroxide for kinetic studies, we first tried the synthesis of Nangia and Benson, and a number of variations, but were unable to obtain yields greater than 5%. We have found, however, that by using ethyl methanesulfonate as starting material, using a dispersing agent, and by distilling the peroxide as formed, a 50% yield of triple-distilled material can readily be obtained in a rapid and simple synthesis. This material is identical with previously prepared ethyl peroxide, as shown by infrared and refractive index, but is of a higher degree of purity. We have studied the purity of ethyl peroxide by infrared and by n.m.r. spectra (following); the material prepared here is 98.5% pure.

Experimental

Ethyl methanesulfonate[5] (62.0 g.), 30% hydrogen peroxide (28.4 g.), and 25 mg. of stearic acid were placed in a three-neck, 300-cc. flask equipped with a mechanical stirrer and thermometer. A solution of 27.3 g. of potassium hydroxide in 30 ml. of water was added dropwise over a period of about 1 hr., keeping the contents of the flask at 0 to 15°. Upon completion of the addition, the ice bath was removed, a simple distillation head with condenser was attached, and the flask was allowed to warm up. After climbing slowly to 60° the flask temperature rose sharply to about 90°, during which time rapid evolution of ethyl peroxide occurred. Additional heating was applied to maintain the temperature at this level for 30 min. The material collected in the trap was transferred to a separatory funnel, neutralized with a few drops of 4 *N* sulfuric acid, and washed three times with distilled water. The crude peroxide was dried over anhydrous sodium sulfate for a day and distilled twice through a 25-cm. micro Vigreux column, yielding 11.1 g. (49.3%) of product, b.p. 62–63°. A comparison of the infrared spectrum of this material with that of standard solutions in carbon tetrachloride of several commonly reported impurities, using a cell of fixed thickness, showed there to be approximately 0.4% water and 1.2% acetaldehyde present. No ethanol or ethyl ether were detectable. All other peaks observed were identical with those reported by Minkoff.[6] The refractive index of the purified ethyl peroxide was $n^{14}D$ 1.3724, agreeing with literature values. Distillation of the peroxide using a more efficient, packed column was found to be less effective for the removal of water and only slightly more effective in reducing the amount of acetaldehyde than the Vigreux column.

The nuclear magnetic spectrum of this material compares favorably with that for propyl peroxide and isopropyl peroxide prepared in these laboratories. Ethyl peroxide had a quartet centered at δ 3.95 and a triplet at 1.18, with a relative intensity of 2:3. Acetaldehyde is detectable by its doublet at δ 2.20, and a comparison of the relative intensities of the β-hydrogens in the two compounds indicates that 1.1% acetaldehyde is present. Other peaks are detected, but in negligible intensity.

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(2) A. Baeyer and V. Villiger, *Ber.*, **33**, 3387 (1900).

(3) R. H. Wiley, U. S. Patent 2,357,298. Yields are given only for crude material boiling at 61–65°. Our experience indicates such material is extremely impure.

(4) P. Nangia and S. W. Benson, *J. Org. Chem.*, **27**, 1882 (1962).

(5) Prepared by the method of H. R. Williams and H. S. Mosher, *J. Am. Chem. Soc.*, **76**, 2987 (1954), in 61% yield. Ethyl methanesulfonate has b.p. 84–85° (9 mm.).

(6) G. J. Minkoff, *Proc. Roy. Soc.* (London), **224A**, 176 (1954).