ethereal layer was separated and dried. Concentration gave 47.5 mg. of material melting at 100–115°. Two recrystallizations from hexane gave 18.7 mg. (0.064 mmole) of 3,4-diphenylphenyl acetate, m.p. 126–128°, identified by mixture melting point and infrared spectral comparison with an authentic sample prepared in 86% yield (m.p. 129.5–130.5°, lit.[9] m.p. 130.0–131.5°) according to the method of Zimmerman and Schuster.[9]

In a similar manner, 91.7 mg. of IV in 5 ml. of acetic acid with 0.2 g. of 10% palladium–carbon was stirred for 1 week under 40–45-lb. of hydrogen pressure. The same processing gave 58.9 mg. of ether-insoluble starting material and 17.2 mg. (m.p. 105–115°) of ether-soluble material. Infrared analysis of the ether-soluble material indicated it was mainly 3,4-diphenylphenyl acetate. Crystallization from hexane gave 7.7 mg., m.p. 124–127°, m.m.p. 125–127°.

Dienone–Phenol Rearrangement of 2-Bromo-4,4-dimethylcyclohexa-2,5-dienone (II). **A. Gas–Liquid Chromatography and Proton Magnetic Resonance Analyses.**—A solution of 1.506 g. (0.00749 mole) of II[4] and 0.705 g. of *p*-toluenesulfonic acid monohydrate in 45 ml. of acetic anhydride was heated at reflux for 2.5 hr. Processing in the usual manner gave 1.719 g. (0.00707 mole) of a liquid. G.l.c. analysis[10] showed only two components (partially resolved) with areas in the ratio of 1.98:1.00. V was identified as the major component by introducing an authentic sample, prepared according to Wegand, *et al.*,[11] and noting which peak was enhanced.

The aromatic proton region in the p.m.r. spectrum (see Fig. 1) of the oil showed a singlet for each *para* proton in V and a partially hidden quartet corresponding to the AB system of *ortho* protons in VI with a first-order coupling constant of 8 c.p.s. Areas under proton signals H_p' and H_o', corresponding to one proton in each molecule, were in the ratio of 1.95:1.00, respectively, in excellent agreement with the ratio obtained by g.l.c. A pure sample of V had singlet aromatic proton signals at 6.80 and 7.25 p.p.m.

B. Hydrolysis and Isolation.—A solution of 1.010 g. (5.00 mmoles) of the bromodienone II and 0.507 g. of *p*-toluenesulfonic acid monohydrate dissolved in 30 ml. of acetic anhydride was refluxed for 10 hr. The dark reaction mixture was poured into 250 ml. of water and shaken for several minutes to hydrolyze most of the acetic anhydride. The aqueous mixture was extracted with two 250-ml. portions of ether, and the combined extracts were washed with dilute sodium bicarbonate, dried, and concentrated to give about 2 ml. of liquid. The liquid was dissolved in 30 ml. of 5% methanolic sodium hydroxide and refluxed for 1 hr. After neutralizing the excess base with acetic acid, the solution was concentrated almost to dryness. The residue was taken up in an ether–water mixture, the ethereal layer separated, and the water fraction washed with ether. The combined organic extracts were dried and concentrated to yield an oil (0.8267 g.) which solidified on standing. Attempts to obtain the pure phenol from this material by recrystallization or sublimation were unsuccessful. The material was chromatographed on a 2 × 45 cm. column packed with silica gel and eluted with 6% ether–hexane. Fractions 1 (250 ml.) and 7 (125 ml.) were blank. Fractions 2 (100 ml.) and 3 (40 ml.) were combined to yield 0.0742 g. (0.37 mmole) of an oil which appeared to be a phenol (presumably 2-bromo-3,4-dimethylphenol) from its infrared spectrum [$\lambda_{\max}^{\mathrm{CS_2}}$ 280 mμ (sharp), 6.20 μ] and monobromination product (following). The oily phenol could not be caused to solidify[12] and definitely was not V (by infrared analysis). Fraction 4 (125 ml., 0.1513 g., 0.75 mmole) appeared, by rough infrared analysis, to be a mixture of approximately equal amounts of the phenols of V and VI. Fraction 5 (250 ml.) yielded 0.2654 g. (1.26 mmole, m.p. 60–70°) of 2-bromo-4,5-dimethylphenol. One recrystallization gave pure phenol (m.p. 77°), identified by infrared comparison and mixture melting point with an authentic sample prepared according to Heiken[14]; $\lambda_{\max}^{\mathrm{KBr}}$ 2.94, 6.19, 11.5, 12.8, 13.6 μ.

Twenty milligrams (0.1 mmole) of the oily phenol in 1 ml. of acetic acid was treated with 25 mg. (0.16 mmole) of bromine in 0.4 ml. acetic acid and the solution allowed to stand in the dark at 25° for 30 min. After pouring into water, neutralizing the acid with sodium bicarbonate, and extracting with ether, 22.8 mg. (0.082 mmole) of an oil was obtained, which solidified to oily needles when seeded with 2,6-dibromo-3,4-dimethylphenol (see below). Recrystallization afforded the dibromophenol as needles, m.p. 33–34°, further identified by infrared analysis.

Dienone–Phenol Rearrangement of 2,6-Dibromo-4,4-dimethylcyclohexa-2,5-dienone (VII).—A solution containing 0.9509 g. (0.0034 mole) of VII[4] and 0.4971 g. of *p*-toluenesulfonic acid monohydrate in 30 ml. of acetic anhydride was heated at reflux for 37.5 hr. Processing as above gave 0.5920 g. of a partially solid material. Fractional crystallization gave 0.1093 g. (0.38 mmole, 11%) of starting material (m.p. 142–144°), further identified by its infrared spectrum. The mother liquors from the crystallization were concentrated and adsorbed onto a chromatographic column (2 × 40 cm.) which had been packed with silica gel and eluted with 8% ether–hexane; 250-ml. fractions were collected. Fractions 1 and 2 gave 0.3417 g. of 2,6-dibromo-3,4-dimethylphenyl acetate containing a small amount of VII as an impurity. Several recrystallizations from petroleum ether (b.p. 40–50°) gave 0.2373 g. (0.74 mmole, 22%) of pure **2,6-dibromo-3,4-dimethylphenyl acetate**, m.p. 57–58°. It was identified by mixture melting point and infrared comparison with an authentic sample (m.p. 57–58°, $\lambda_{\max}^{\mathrm{KBr}}$ 5.60, 8.35, 9.68 μ) prepared by acetylation of 2,6-dibromo-3,4-dimethylphenol.[15]

Anal. Calcd. for $C_{10}H_{10}Br_2O_2$: C, 37.30; H, 3.13. Found: C, 37.47; H, 3.06.

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[9] H. E. Zimmerman and D. I. Schuster, *J. Am. Chem. Soc.*, **84**, 4527 (1962).

[10] G.l.c. analyses were made on an F & M Model 300 chromatograph using a 15-ft. column packed with 8% 550 silicon oil on 60–80-mesh Chrom P, programmed over 140–190°.

[11] F. Wegand, K. Vogelback and K. Zimmerman, *Ber.*, **80**, 391 (1947).

[12] Hunsberger, *et al.*,[13] have reported that 2-bromo-3,4-dimethylphenol exists as an oil.

[13] I. M. Hunsberger, D. Lednicer, H. S. Gutowsky, D. L. Bunker, and P. Taussig, *J. Am. Chem. Soc.*, **77**, 2466 (1955).

[14] K. Heiken, *Angew. Chem.*, **52**, 236 (1939).

[15] E. von Auwers, *Ann.*, **344**, 171 (1906).

The Structure of Carolic Acid

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Carolic acid,[1] a metabolite of *Penicillium charlesii* G. Smith, possesses the molecular formula $C_9H_{10}O_4$. Consideration of the reactions of the acid in aqueous solution led Clutterbuck,[2] *et al.*, to suggest that the compound resembled the α-acyltetronic acids and could best be represented as a hydrated form (I). It was postulated that the crystalline compound was derived from the hydrated form by loss of water and might possess structure II. Clutterbuck, *et al.*,[2] found that in dry anisole, carolic acid contained no active hydrogen, whereas in pyridine one active hydrogen atom was shown to be present; in order to explain this observation they postulated that the —$COCH_2$— group of the seven-membered ring in II may undergo enolization to —C(OH)=CH— in pyridine. Duncanson[3] has commented that the infrared spectrum of carolic acid under anhydrous conditions suggests that the structure is more closely related to those of the alkyl ethers of the tetronic acids than to the tetronic acids themselves.

A study of the n.m.r. spectrum[4] of carolic acid now confirms its formulation as II. Unlike those of typical acyltetronic acids[5] the spectrum shows no absorption

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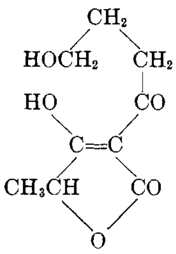
[1] P. W. Clutterbuck, W. N. Haworth, H. Raistrick, G. Smith, and M. Stacey, *Biochem. J.*, **28**, 94 (1934).

[2] P. W. Clutterbuck, H. Raistrick, and F. Reuter, *ibid.*, **29**, 300 (1935).

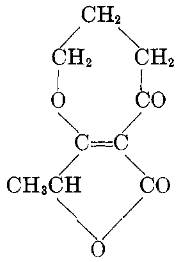
[3] L. A. Duncanson, *J. Chem. Soc.*, 1207 (1953).

[4] Measured on Varian A-60 spectrometer in deuteriochloroform solution with tetramethylsilane as internal standard (δ = 0.00 p.p.m.).

[5] L. J. Haynes and J. R. Plimmer, unpublished observations.



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-C-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_3C-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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[1] Louisiana State University, Department of Chemistry, Baton Rouge, La.

[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).