

under reflux for 6 hr., cooled, and diluted with ether and water. The organic layer was washed with water, dried and evaporated to dryness. The residue was acetylated by being allowed to stand overnight at room temperature with 10 cc. of pyridine and 10 cc. of acetic anhydride. The product was isolated with ether in the usual way and chromatographed on 25 g. of Merck "acid-washed" alumina. The fractions eluted with petroleum ether-benzene (4:1) on crystallization from methanol yielded 290 mg. of the pentaene acetate IV with m.p. 118–120°. The analytical sample showed m.p. 132–133°, $[\alpha]_D + 65^\circ$, ν_{\max} 1750 (phenyl acetate), 1620 and 890 cm^{-1} (terminal methylene), λ_{\max} 239 $\text{m}\mu$ ($\log \epsilon$ 4.22) (iso-octane).

Anal. Calcd. for $\text{C}_{23}\text{H}_{28}\text{O}_2$: C, 82.10; H, 8.39. Found: C, 82.11; H, 8.39.

Adduct V from 17-isopropenyl- $\Delta^{1,3,5(10),16}$ -estratetraen-3-ol acetate (IV) and maleic anhydride. A solution of 60 mg. of the pentaene acetate IV and 60 mg. of maleic anhydride in 6 cc. of benzene was boiled under reflux for 6 hr. Isolation as previously and crystallization from ether gave 35 mg. of the adduct V with m.p. 178–182°. Further crystallization from ether gave the analytical specimen with m.p. 182–184°, $[\alpha]_D + 83^\circ$, ν_{\max} 1850, 1780 cm^{-1} (5-membered cyclic anhydride) and 1760 cm^{-1} (phenyl acetate), λ_{\max} 268 $\text{m}\mu$ ($\log \epsilon$ 2.98) (95% ethanol).

Anal. Calcd. for $\text{C}_{27}\text{H}_{30}\text{O}_5$: C, 74.63; H, 6.96. Found: C, 74.44; H, 7.02.

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Improved Yields in the Preparation of Diacetyl Peroxide

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In connection with some studies on the oxidation of cyclohexene¹ and on the stability of acyloxy radicals it was necessary to prepare reasonably large amounts of pure diacetyl peroxide in the solid state. The several methods of preparation available in the literature were found unsuitable. Thus, Shanley's method² is suitable for small amounts only, Walker's method³ appeared too dangerous for large scale use, particularly in warm climates, and a patented method⁴ involved an unsuitable solvent. The well-known method of Gambarjan,⁵ outlined by Shirley⁶ gave variable and poor yields. However, by modifying Gambarjan's method it was possible to prepare diacetyl peroxide in 79%

yield, and the peroxide obtained was of excellent purity. Although Kuhn⁷ recommends using the peroxide within 24 hours when it is prepared by Gambarjan's method, we were able to store the peroxide in Dry Ice and use it a week later. However, we do not recommend this as a general practice. Where it is necessary to prepare the solid peroxide for subsequent investigation in a particular solvent we recommend adding the solvent to the peroxide before removing the peroxide container from its Dry Ice surroundings.

EXPERIMENTAL

A solution of 87 g. (0.723 mole) acetic anhydride in 450 ml. of ether, freshly distilled after standing over sodium, was placed in a 1 liter Erlenmeyer flask in an ice bath. To the flask was added 43.5 g. (0.558 mole) of sodium peroxide in one portion. The mixture was stirred mechanically and distilled water (150 ml.) was added to it dropwise until all of the sodium peroxide had dissolved. The addition of the water took approximately 10 hr. and was controlled so as to keep the temperature of the mixture below 5° and to avoid, as much as possible, the evolution of oxygen. After the addition was finished the ether layer was separated and the aqueous layer was extracted with two 100-ml. portions of ether. The combined ether solutions were washed with two 100-ml. portions of 1% sodium bicarbonate solution to remove acetic acid. The ether solution was then dried over calcium chloride for 2 hr., carefully decanted into a tared, standard taper flask, which was equipped with a calcium chloride tube, and allowed to stand in a Dry Ice-alcohol slurry overnight. A large crop of solid peroxide crystals formed. This was not removed. Instead, the flask was raised slightly above the rim of the Dewar vessel, and the ether was removed at low pressure.

Iodimetric assay⁸ gave a peroxide content of 98.97%. Small amounts of the solid peroxide were removed from the flask with a porcelain spatula for assay and quickly transferred to a weighing bottle containing a known weight of isopropyl alcohol. Large amounts of solid peroxide were never removed from the flask; instead the peroxide was dissolved in the required solvent and used in a manner to be described in a later publication.

Although this procedure takes longer than Gambarjan's⁵ it has been found to be much more reliable and consistent in its results. For example, two representative runs using the quantities above gave 39.6 g. (79% yield) and 39.2 g. (77.8% yield), the yields being based on acetic anhydride. In contrast, by following Gambarjan's procedure, as described by Shirley,⁶ yields varying from 9.1 to 43.3% were obtained in 5 attempts.

No trouble was experienced at any time during preparations as outlined above. During the removal of the ether by pumping and during storage and handling of the flask containing the solid peroxide the apparatus was shielded by safety screens. The solid was never allowed to approach its melting point and was never brought into contact with anything but glass or porcelain surfaces. Whenever possible the apparatus containing the solid peroxide was handled with tongs.

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