ether, washed with 10% H_2SO_4 solution, saturated $NaHCO_3$ solution, and brine, dried ($MgSO_4$), and concentrated under reduced pressure to yield a 2:1 mixture of butenolides **26** and **25** (1.5 mg, 0.006 mmol, 72% crude).

Butenolides 25 and 26 via Triazolidinediones 27. To a solution of ene adducts **27**[12] (84 mg, 0.198 mmol) in dichloromethane (0.8 mL) was added triethylamine (40 mg, 0.396 mmol) and acetic anhydride (40 mg, 0.396 mmol). The resultant bright yellow solution was stirred at room temperature for 6 h, diluted with ether, washed with saturated $NaHCO_3$ solution and brine, dried ($MgSO_4$), and concentrated under reduced pressure. The crude product when subjected to preparative layer chromatography (1:1 hexanes–ethyl acetate) afforded a 2:1 mixture of butenolides **25** and **26** (29 mg, 0.116 mmol, 59%).

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Registry No. 1, 70003-96-2; 4, 76248-72-1; 5, 76215-55-9; 6, 76248-73-2; 7, 76248-74-3; 8a (isomer 1), 76215-56-0; 8a (isomer 2), 76215-57-1; 8b (isomer 1), 76215-58-2; 8b (isomer 2), 76215-59-3; 9c (isomer 1), 76215-60-6; 9c (isomer 2), 76248-75-4; 16, 71075-17-7; 17, 76215-61-7; 18, 76215-62-8; 19, 76248-76-5; 20, 76215-63-9; 21, 76215-64-0; 21 methyl ester, 76215-65-1; 22, 76215-66-2; 23, 76215-67-3; 24, 76232-17-2; 25, 76215-68-4; 26, 76215-69-5; 27 (isomer 1), 74561-77-6; 27 (isomer 2), 74542-30-6; 28 (isomer 1), 76215-70-8; 28 (isomer 2), 76248-77-6; 29, 76232-18-3; 30, 76215-71-9; 31, 76248-78-7; α-(γ-butyrolactonylidene)triphenylphosphorane, 34932-07-5; α-(diethylphosphono)-γ-butyrolactone, 2907-85-9; diphenyl diselenide, 1666-13-3; benzeneselenenyl chloride, 5707-04-0; 14 (isomer 1), 76215-72-0; 14 (isomer 2), 76215-73-1; α-(phenylthio)-γ-butyrolactone, 35998-30-2.

Notes

2,4-Dinitrophenyl Dihydrogen Phosphate: A New Synthesis of Its Mono-2,6-lutidinium Salt

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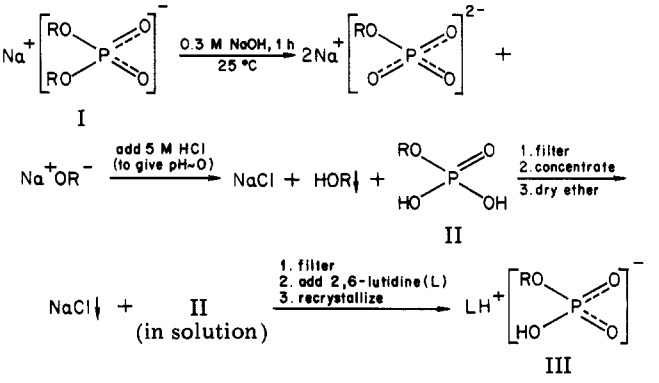
2,4-Dinitrophenyl phosphate[1] (2,4-DNPP) has been the focus of attention in both nonenzymatic[2-14] and enzymatic[15-20] studies of phosphate esters, the latter studies relating in particular to *E. coli* alkaline phosphatase. In consequence there has been active interest in suitable methods for its preparation. Of the several methods reported,[2-7] not all are satisfactory, as has been described.[4,6,8]

Scheme I



R = 2,4-dinitrophenyl

Two well worked out procedures[4,6] are relatively time consuming.

In connection with our studies on phosphate ester hydrolysis we have had need for 2,4-DNPP and for this purpose have developed a simple preparative procedure which we believe will be of general use. The method starts from the easily prepared[10] bis(2,4-dinitrophenyl) phosphate[21] and is based on the observation that in highly alkaline aqueous solution the diester hydrolyzes much more rapidly than the monoester, with a rate difference of about 80-fold at pH 13.5 and 25 °C. For the latter conditions we allow the diester to hydrolyze for ~6 half-lives ($k = 1.2 \times 10^{-3}$ s^{-1}; $6t_{1/2} = 62$ min); this relatively rapid hydrolysis is then quenched by addition of acid. Separation of the monoester from the other components is readily achieved. The overall procedure is summarized by Scheme I; details are in the Experimental Section.

Experimental Section

The method of Bunton and Farber[10] is used to prepare bis(2,4-dinitrophenyl) phosphate as the pyridinium salt (yield ~ 75%). The pyridinium ion is exchanged for Na^+ with use of cation-exchange resin (Dowex 50W X8) in the Na^+ form. For

(1) A complete name for the free acid is 2,4-dinitrophenyl dihydrogen phosphate; the term "2,4-dinitrophenyl phosphate" is commonly used, as here, to include the free acid as well as the monoanion and dianion.
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(21) The free acid is more properly called bis(2,4-dinitrophenyl) hydrogen phosphate.

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maximum yield the resin is soaked in methanol before use and a methanolic solution of the diester is used. After ion exchange, the solution is concentrated by rotary evaporation (~30 °C). When this solution is cooled (to ~0 °C) sodium bis(2,4-dinitrophenyl) phosphate (I) is obtained as a bright yellow solid. It is recrystallized from ethanol (yield ~85%).

Anal. Calcd for $C_{12}H_6N_4O_{12}PNa$: C, 31.9; H, 1.34; N, 12.4; P, 6.85; Na, 5.08. Found: C, 32.0; H, 1.33; N, 12.2; P, 6.68; Na, 4.87.

Sodium bis(2,4-dinitrophenyl) phosphate (I) (1 g) is rapidly dissolved in ~50 mL of aqueous 0.30 M NaOH. The resulting solution of pH ~13.5 is held at 25 ± 2 °C for 1 h (~6 half-lives), after which ~15 mL of aqueous 5 M HCl is added to lower the pH to ~0. The reaction mixture is cooled (ice bath) and the 2,4-dinitrophenol is removed by filtration. The filtrate, containing the monoester as the free acid (II), is concentrated (rotary evaporator, ~35 °C) to a thick syrup. The NaCl is now precipitated by adding dry ether. After filtration, the ether solution is stirred while 2,6-lutidine is added dropwise until the solution develops a permanent bright yellow color (~0.26 mL required). The resulting pale yellow solid is collected and washed with ether. Recrystallization from hot ethanol gives the required 2,6-lutidinium 2,4-dinitrophenyl hydrogen phosphate (III) as a white solid. A second crop may be obtained by concentrating the ethanolic solution (total yield, ~65%).

Anal. Calcd for $C_{13}H_{14}N_3O_8P$: C, 42.1; H, 3.80; N, 11.3; P, 8.34. Found: C, 41.9; H, 3.68; N, 11.2; P, 8.29.

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Registry No. I, 76215-44-6; II, 2566-26-9; III, 6186-33-0; bis(2,4-dinitrophenyl)phosphate pyridinium salt, 76215-45-7; 2,6-lutidine, 108-48-5.

Thermal Decarboxylation of 3,17-Dioxo-4β,5-epoxy-5β-androstan-19-oic Acid and Some Transformations of the Derived Product

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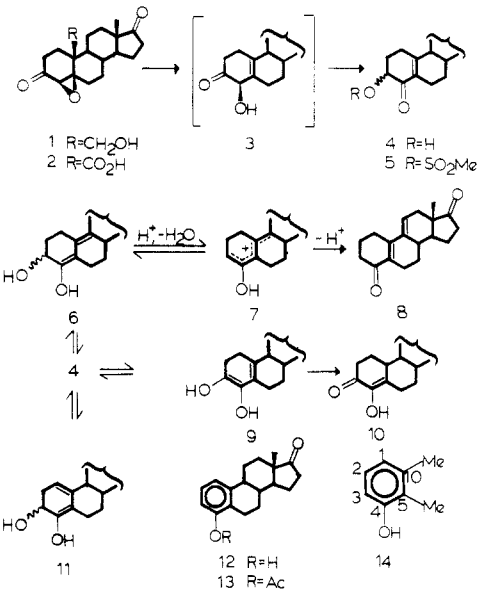
We have reported our results of reactions in which the C-10 hydroxymethyl group of 5β,6β-steroidal epoxides[1] is eliminated on epoxide opening by boron trifluoride. The observation[2] that β,γ-epoxy acids can be made to undergo thermal decarboxylative elimination under relatively mild conditions (refluxing toluene) prompted us to attempt a similar reaction with the acid **2**. It was hoped that the neutral conditions employed in this reaction would allow for the isolation of the allylic alcohol **3**, a compound of interest to us since we have postulated it as an intermediate in the enzymatic conversion[3] of the epoxide **1** to estradiol.

The acid **2** was prepared by Jones oxidation of the alcohol **1**. It was found to be stable in refluxing toluene and xylene but in decalin it reacted to give two chromatographically homogeneous products. The minor product (9%) was estrone and the major product (79%), although



tautomeric (*m/e* 288, M^+) with the desired allylic alcohol **3**, exhibited absorptions (IR 1655 and 1619 cm^{-1}; UV 247 nm) indicative of an α,β-unsaturated ketone, namely, **4**. The ^1H NMR only showed an apparent quartet for the 3-H, but the ^{13}C NMR ($CDCl_3$) indicated that it had been obtained as a mixture of epimers [the more readily assignable downfield signals were 219.92 (C-17), 182.23 and 181.58 (C-4), 159.31 and 158.26 (C-10), 129.67 C-5), 71.91 and 71.83 (C-3)].

It would appear that the allylic alcohol **3** was initially formed but isomerized to the α,β-unsaturated ketone **4** under the reaction conditions. As **4** was stable to further reflux in decalin, the estrone formed may have arisen by dehydration of the allylic alcohol.

Since this 3-hydroxy-$\Delta^{5(10)}$-4-one system is novel in steroid chemistry, we briefly examined some of its properties. With base, **4** was found to isomerize to the diosphenol **10**. This compound exhibited absorptions in the UV at 276 nm and in the IR at 1670 and 1650 cm^{-1} which are consistent with this structure.

Under acidic conditions (concentrated $HClO_4$, THF) it was found to undergo dehydration to give a compound (*m/e* 270, M^+) whose IR spectrum indicated the presence of an αβ,γδ-unsaturated ketone (1655, 1605, 1590 cm^{-1}). Since the ^1H NMR spectrum showed a single olefinic proton (δ 6.18) which was coupled with an adjacent center, it was assigned structure **8**. Although the λ_{max} (289 nm) was somewhat lower than may be expected[4] (308 nm), the relatively large extinction coefficient (23 000) is consistent with a heteroannular diene system.

The acid- or base-catalyzed reactions of **4** would be expected to proceed via the enols (or enolates) corresponding to **6**, **9**, or **11**. Under basic conditions, the enone **4** isomerizes via the enolate of **9** to the acidic diosphenol **10** which would exist as an anion in the basic solution. However, under acidic conditions, it appears that the heteroannular dienol **6** predominates or at least that the subsequent acid-catalyzed dehydration [**6** → **7** → **8**] draws any possible equilibria with the other enols, **9** or **11**, in this direction. This would mean that the enol **9**, if formed, isomerizes back to **4** more rapidly than protonation at C-10 since the diosphenol was found to be stable under these reaction conditions. The proposed dehydration sequence draws some support from the observation[5] that the 3β-acetoxy-

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