involving benzylation of 2,6-diaminopurine, then Schiemann reaction followed by ether extraction of 9-benzyl-2-fluoroadenine, and finally removal of the benzyl group with metallic sodium in liquid ammonia.

In view of existing precedents for the introduction of fluorine into aromatic systems by way of diazotization in anhydrous hydrogen fluoride,[8] it was decided to apply this method to 2,6-diaminopurine even though no such reactions of aminopurines were found in the literature. We found the addition of solid sodium nitrite to a solution of 2,6-diaminopurine in anhydrous hydrogen fluoride to be a facile and convenient procedure resulting in a 22% yield of pure 2-fluoroadenine. The product is a hygroscopic powder with the extent of hydration dependent upon crystalline structure, purity, and external atmospheric conditions.

Experimental Section

The ultraviolet spectra were determined using a Cary Model 11 spectrophotometer. Paper chromatograms were performed by the descending technique on Whatman No. 1 paper, using ultraviolet light for visualization.

2-Fluoroadenine.—To 150 ml of magnetically stirred anhydrous hydrogen fluoride (Matheson) in a polyethylene beaker immersed in an ice bath was added in portions 50.0 g (0.30 mole) of 2,6-diaminopurine hydrate.[9,10] Sodium nitrite (23.0 g, 0.33 mole) was added in portions to the stirred mixture at 0° over a 75-min period. The mixture was stirred for an additional 5 min and then purged with nitrogen for 20 min at 0°. The ice bath was removed, and the nitrogen purge continued. After evaporation of the hydrogen fluoride, the weight of 2-fluoroadenine was 74.0 g. This material was shown to contain approximately 30% ash. The ash level was reduced to below 0.3% by treating the product with distilled water (50 ml/g) five times in a Waring Blendor. To remove residual color, the product (19.0 g) was further purified by dissolving it in 11.5 l. of boiling water, treating the solution with 20 g of Darco KB, filtering, and concentrating the filtrate to dryness *in vacuo*. The residue was treated with water in the Blendor, ground, washed with ether, and air dried to give 11.2 g (22%) of analytically pure 2-fluoroadenine. Paper strip chromatography and ultraviolet absorption data corresponded with the reported values.[4]

Registry No.—2-Fluoroadenine, 18916-91-1.

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A Convenient Synthesis of Hydroxymethyldiphenylphosphine Oxide and Substituted α-Hydroxybenzyldiphenylphosphine Oxides

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There are several routes for the preparation of hydroxymethyldiphenylphosphine oxide and its α-substituted derivatives. Those based on diphenylphosphine[2-5] (eq 1 and 2) have the obvious disadvantage

$$Ph_2PH \xrightarrow{PhCHO} Ph_2PCH(OH)Ph \xrightarrow{AcOOH} Ph_2P(O)CH(OH)Ph \quad (1)$$

$$Ph_2PH \xrightarrow{PhCHO,\ HCl} [Ph_2P(CH(OH)Ph)_2]Cl \xrightarrow{OH^-} Ph_2P(O)CH(OH)Ph \quad (2)$$

that an oxidatively unstable, malodorous starting material that requires prior preparation is used. Miller and coworkers[6,7] prepared various α-mono- and disubstituted α-hydroxymethyldiorganophosphine oxides by the base-catalyzed addition of secondary phosphines oxides to aldehydes and ketones (eq 3). The drawback

$$R_2P(O)H + R'CHO \xrightarrow{NaOEt} R_2P(O)CH(OH)R' \quad (3)$$
$$R = PhCH_2,\ n\text{-}C_8H_{17},\ Ph$$

of this procedure is that it requires prior preparation of the secondary phosphine oxide. Finally, a more direct route, reported much earlier by Conant and coworkers[8] and confirmed by Miller *et al.*,[6] involves the reaction of diphenylchlorophosphine with benzaldehyde in glacial acetic acid. This procedure, however, appears to give only poor (27% in the case of benzaldehyde) yields of product.

We have found that compounds of the type $Ph_2P(O)CH_2OH$, $Ph_2P(O)CH(OH)Ar$ (Ar = Ph, *p*-ClC_6H_4, *p*-MeC_6H_4 and *p*-$NO_2C_6H_4$) and $Ph_2P(O)CH(OH)CCl_3$ may be prepared very simply and in good yield by the reaction of the commercially available diphenylchlorophosphine,[9] the respective aldehyde and concentrated hydrochloric acid. With *p*-anisaldehyde, the product isolated was the α-chloro derivative (eq 4). The corresponding α-hydroxy compound was prepared, however, when diphenylphosphine oxide in aqueous sulfuric acid was substituted for diphenylchlorophosphine in hydrochloric acid. This α-hydroxy compound was converted into the α-chloro compound on reaction with hydrochloric acid (eq 5 and 6). The greater lability

$$Ph_2PCl + p\text{-}MeOC_6H_4CHO \xrightarrow{HCl} Ph_2P(O)CH(Cl)C_6H_4OMe\text{-}p \quad (4)$$

$$Ph_2P(O)H + p\text{-}MeOC_6H_4CHO \xrightarrow{H_2SO_4} Ph_2P(O)CH(OH)C_6H_4OMe\text{-}p \quad (5)$$

$$Ph_2P(O)CH(OH)C_6H_4OMe\text{-}p \xrightarrow{\text{concd HCl}} Ph_2P(O)CH(Cl)C_6H_4OMe\text{-}p \quad (6)$$

of the hydroxy group in the *p*-anisaldehyde adduct might be expected on the basis of resonance forms which can be drawn for the electron releasing methoxy group.

We believe the general reaction is one which proceeds

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via the *in situ* formation of diphenylphosphine oxide (eq 7) rather than involving direct addition of diphenylchlorophosphine to the carbonyl group.

$$Ph_2PCl + H_2O \longrightarrow Ph_2P(O)H + HCl \xrightarrow{RCHO} Ph_2P(O)CH(OH)R \quad (7)$$

Aliphatic aldehydes (*e.g.*, butyraldehyde) slowly decomposed and benzophenone was unreactive under the reaction conditions employed.

Experimental Section

Hydroxymethyldiphenylphosphine Oxide.—A 1-l. flask, previously flushed with nitrogen and filled with 19.5 g (0.113 mol) of diphenylchlorophosphine, 200 ml of concentrated hydrochloric acid and 200 ml of 37% aqueous formaldehyde solution (2.47 mol, a 22-fold excess) was heated on a steam bath overnight. Evaporation of the reaction mixture at reduced pressure left an oil which was neutralized with aqueous sodium bicarbonate and extracted with chloroform. The dried chloroform extracts were evaporated and the resulting residue was crystallized from benzene–heptane to give 16.6 g (63%) of product, mp 134°. Another recrystallization from benzene gave material with mp 136.0–136.5° (lit.[3] mp 137–139°). A mixture melting point with authentic material[3] was not depressed.

α-Hydroxy-β,β,β-trichloroethyldiphenylphosphine Oxide.—To a stirred solution of 3.64 g (22 mmol) of chloral hydrate in 44 ml of concentrated hydrochloric acid in an ice bath under nitrogen was added 4.88 g (22 mmol) of diphenylchlorophosphine. The flask was sealed and stirred at room temperature for 17 hr; then 150 cc of ice water was added. The aqueous acid solution was decanted from the solids. The solids were washed with water, then recrystallized from methanol–water to give 2.21 g of product. A second crop weighed 0.29 g (total yield 32.5%). Recrystallization gave an analytical sample, mp 169.5–170.5° (lit.[10] mp 171.5–172.5°). *Anal.* Calcd for $C_{14}H_{12}O_2Cl_3P$: C, 48.10; H, 3.46; Cl, 30.43. Found: C, 48.36; H, 3.47; Cl, 30.50.

Substituted α-Hydroxybenzyldiphenylphosphine Oxides. Procedure A.—The identical procedure was used as above, substituting 22 mmol of the respective aldehyde for the chloral hydrate.

Procedure B was similar to procedure A, but the reactants were combined at room temperature and placed on the steam bath without stirring overnight. The following products were obtained: **α-hydroxybenzyldiphenylphosphine oxide** [mp 177–178° (lit.[6] mp 178–179.5°); 85% (A), 75% (B) yields]; **α-hydroxy-p-chlorobenzyldiphenylphosphine oxide** [mp 181.5–183.0°, recrystallized to constant melting point (lit. mp 188°,[2] 168–170°;[4] 64% (A), 60% (B) yields) (*Anal.* Calcd for $C_{19}H_{16}ClO_2P$: C, 66.58; H, 4.71; Cl, 10.34. Found: C, 66.74; H, 4.83; Cl, 10.64)]; **α-hydroxy-p-methylbenzyldiphenylphosphine oxide** [mp 152.5–155.0°; 86% (A), 61% (B) yields (*Anal.* Calcd for $C_{20}H_{19}O_2P$: C, 74.52; H, 5.94. Found: C, 74.28; H, 5.83)]; **α-chloro-p-methoxybenzyldiphenylphosphine oxide** [mp 181–182°; 30% crude (A), 65% (B) yields (*Anal.* Calcd for $C_{20}H_{18}ClO_2P$: C, 67.33; H, 5.08; Cl, 9.94. Found: C, 67.39; H, 5.16; Cl, 9.89)]; **α-hydroxy-p-nitrobenzyldiphenylphosphine oxide** [mp 191.5–193.0°; 62% (A), 73% (B) yields (*Anal.* Calcd for $C_{19}H_{16}NO_4P$: C, 64.59; H, 4.57. Found: C, 64.70; H, 4.65)].

α-Hydroxy-p-methoxybenzyldiphenylphosphine Oxide.—To a stirred mixture of 20 ml of water, 10 ml of dioxane and 14 ml of concentrated sulfuric acid in an ice bath under nitrogen was added 2.72 g (20 mmol) of *p*-anisaldehyde followed by 4.04 g (20 mmol) of diphenylphosphine oxide. The mixture was stirred for 5 min until homogeneous, then the ice bath was removed and stirring continued for 22 hr at room temperature. Water (60 ml) was added and the precipitate was filtered off and washed with water, then recrystallized from methanol, yielding in three crops, 5.65 g (84% yield). Recrystallization gave an analytical sample, mp 160–162°. *Anal.* Calcd for $C_{20}H_{19}O_3P$: C, 71.00; H, 5.66. Found: C, 70.84; H, 5.66.

Conversion of α-Hydroxy-p-methoxybenzyldiphenylphosphine Oxide into α-Chloro-p-methoxybenzyldiphenylphosphine Oxide.—In a flask was placed 1.69 g of the hydroxy compound and 20 ml of concentrated hydrochloric acid. The flask was sealed with a balloon and heated on the steam bath for 15 hr. The mixture was cooled and diluted with an equal volume of water, refrigerated 30 min, then the acid solution was decanted off. The residue was rinsed with water, then recrystallized from 20 ml of methanol, affording 0.97 g of the chloro compound, mp 181–182°; the mixture melting point was undepressed. The infrared spectra of these products were in agreement with the structures given.

Registry No.—Hydroxymethyldiphenylphosphine oxide, 884-74-2; $C_{19}H_{16}ClO_2P$, 18872-82-7; $C_{20}H_{19}O_2P$, 18872-83-8; $C_{20}H_{18}ClO_2P$, 18872-84-9; $C_{19}H_{16}NO_4P$, 18872-85-0; $C_{20}H_{19}O_3P$, 18872-86-1.

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Electron-Transfer Polymers. XXXVI. Acetylated Trimethylhydroquinone Derivatives

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Among the many redox polymers that may be conceived[2] those from hydroquinone tetrasubstituted with alkyl groups have seemed particularly interesting because of the chemical stability and low potential expected of them. Because a low-potential polymer is difficult to maintain unprotected in the reduced form we designed, prepared, and reported a durobenzoquinonyl glycol,[3a] the monomer of which is related to tocopherol. In the subsequent investigations of this synthesis it has turned out that in preparing 3-acetoxy-6-hydroxy-2,4,5-trimethylbenzyl chloride (XIV) according to the method of Smith and Carlin,[3b] another compound could be isolated, namely, 2-acetoxy-5-hydroxy-3,4,6-trimethylbenzylchloride (XV). Compound XV is less soluble in ether than XIV and may be separated in this way.[4] The mixture melting point of XIV (149–151°) and XV (149–150°) was 147–150°; the nmr of XIV showed three peaks and that of XV four peaks around τ 7.6–8.0. The determination of structure, carried out by comparing nmr spectra of these and reference compounds, is discussed below (see Chart I).

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