ir (KBr) 1680 cm^{-1} (CO); uv max (CH_3CN) 231 nm (ε 33,900), 255 (sh) (17,500), 317 (2740); nm ($CDCl_3$) δ 1.33 (t, 6, 2 CH_3), 3.43 (s, 3, NCH_3), 4.12 (m, 1, $CH(CH_3)_2$), 4.88 (s, 1, H-3), 7.2–7.8 ppm (m, 8, aromatic); molecular ion *m/e* 342 (calcd 342).

Anal. Calcd for $C_{19}H_{19}ClN_2O_2$: C, 66.56; H, 5.58; N, 8.17; Cl, 10.34. Found: C, 66.60; H, 5.84; N, 8.04; Cl, 10.43.

The structure of **4** was confirmed by a synthesis from the corresponding 3-chloro compound **2**[4] as shown.

A solution of 3,7-dichloro-1,3-dihydro-1-methyl-5-phenyl-2*H*-1,4-benzodiazepin-2-one[4] (**2**, 164 mg, 0.50 mmol) in isopropyl alcohol (20 ml) was heated on a steam bath for 20 min. The solution was evaporated to dryness. Crystallization of the residue from ether–pentane afforded 112 mg (65%) of **4** as prisms, mp 210–211°, identical with that prepared above by ir, tlc, and mixture melting point.

7-Chloro-1,3-dihydro-3-ethoxy-5-phenyl-2*H*-1,4-benzodiazepin-2-one (6).[12]—To a solution of 7-chloro-4,5-epoxy-5-phenyl-1,3,4,5-tetrahydro-2*H*-1,4-benzodiazepin-2-one[2] (**5**, 574 mg, 2.0 mmol) in ethyl alcohol (500 ml) was added an aqueous solution of ferrous sulfate heptahydrate (834 mg, 3.0 mmol, in 10 ml of water). The mixture was stirred at room temperature for 20 hr under nitrogen. Solvent was evaporated. The residue was partitioned between methylene chloride and brine. The methylene chloride layer was washed with water, dried (Na_2SO_4), and evaporated to dryness. The residue was applied to a column of 50 g of Florisil with methylene chloride. Elution with 1.5 l. of ethyl acetate followed by 500 ml of acetone afforded pure **6** (R_f 0.37 on silica gel tlc, using ether). Crystallization from methylene chloride–ether afforded 180 mg (28%) of colorless flakes, mp 222–224°, identical (tlc and mixture melting point) with a sample of **6** prepared by the literature procedure.[12]

7-Chloro-1,3-dihydro-3-hydroxy-5-phenyl-2*H*-1,4-benzodiazepin-2-one (7).[12] **A. With Aqueous Ferrous Sulfate.**—To a solution of 7-chloro-4,5-epoxy-5-phenyl-1,3,4,5-tetrahydro-2*H*-1,4-benzodiazepin-2-one[2] (**5**, 143 mg, 0.50 mmol) in tetrahydrofuran (100 ml) was added an aqueous solution of ferrous sulfate heptahydrate (208 mg, 0.75 mmol, in 20 ml of water). The mixture was stirred under nitrogen at room temperature for 3 days. The solvent was evaporated. The residue was partitioned between methylene chloride and saturated brine. The methylene chloride layer was washed with water, dried (Na_2SO_4), and evaporated to dryness. Crystallization of the residue from ether afforded 100 mg (69%) of **7** as colorless prisms, mp 208–210°. This material was found identical (ir, tlc, mixture melting point) with a sample of **7** prepared by the known[12] procedure.

B. With Aqueous Ferric Chloride.—To a solution of **5** (144 mg, 0.50 mmol) in tetrahydrofuran (150 ml) was added an aqueous solution of ferric chloride hexahydrate (Baker reagent grade, 0.75 mmol, in 20 ml of water). The mixture was stirred under nitrogen at room temperature for 7 days. The product was isolated in the same manner as described above in A. The yield of **7**, isolated as colorless prisms from ether, was 94 mg (65%), mp 206–208°. It was identified by ir, tlc, and mixture melting point.

C. With Ferric Chloride Hexahydrate.—To a solution of **5** (1.44 g, 5.0 mmol) in tetrahydrofuran (800 ml) was added solid ferric chloride hexahydrate (2.03 g, 7.5 mmol). The mixture was stirred under nitrogen at room temperature for 1 day. Isolation of the product in the same manner as described in A afforded 580 mg (40%) of **7**, identified by ir, tlc, and mixture melting point.

Stability of 7-Chloro-1,3-dihydro-1-methyl-5-phenyl-2*H*-1,4-benzodiazepin-2-one 4-Oxide (8) toward Ferrous Sulfate.—To a solution of 1.5 g (5.0 mmol) of **8** in 1 l. of isopropyl alcohol was added an aqueous solution of ferrous sulfate heptahydrate (2.09 g, 7.5 mmol, in 50 ml of water). After 2 days of stirring at room temperature, under nitrogen, tlc indicated no signs of reaction. After evaporation of solvent and partitioning the residue between methylene chloride and water, **8** was quantitatively recovered.

Acknowledgment.—We thank Dr. R. P. W. Scott and his staff in our Physical Chemistry Department, in particular, Dr. W. Benz for mass spectra, Dr. F. Scheidl for elemental analyses, Dr. V. Toome for uv measurements, Mr. S. Traiman for ir spectra, and Dr. T. Williams for nmr spectra.

Registry No.—**1**, 24605-70-7; **2**, 23433-96-7; **3**, 846-50-4; **4**, 42077-69-0.

Addition of Trimethyl Phosphite to β-Nitrostyrene

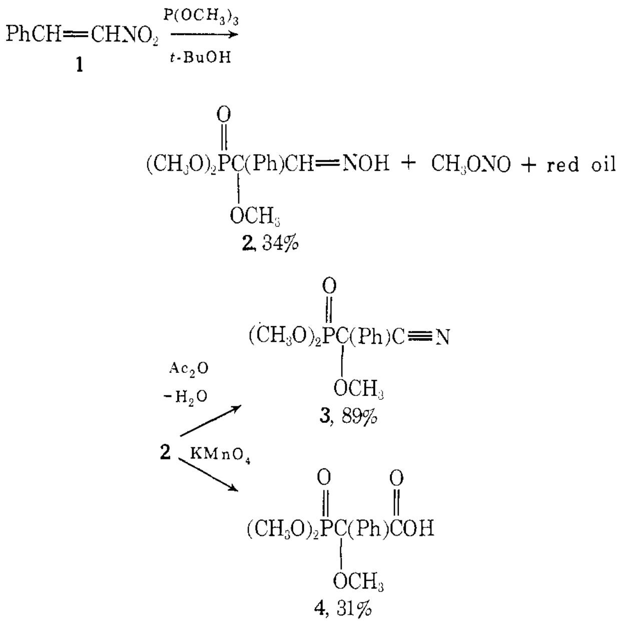
William E. Krueger* and John R. Maloney

Department of Chemistry, State University of New York, College of Arts and Science, Plattsburgh, New York 12901

Received June 26, 1973

In connection with a general study of the deoxygenation of nitroalkenes with trivalent phosphorus compounds, β-nitrostyrene (**1**) was treated with trimethyl phosphite in *tert*-butyl alcohol at room temperature. The exothermic reaction formed a white solid in 34% yield. This solid was not the product of the intermediate nitrene expected of deoxygenation, nor was it similar to the product of the reaction of β-nitrostyrene with triethyl phosphite.[1] The chemical and physical data support **2** as the structure of this compound; the other products of this reaction include an unidentified red oil and an undetermined amount of methyl nitrite[2] (Chart I).

Chart I



Elemental analyses gave an empirical formula of $C_{11}H_{16}NO_5P$, a 1:1 adduct of the starting materials, and was in agreement with the mass spectrum which showed a molecular ion of M^+ 273. The presence of the phosphonate ester group was established by the ^{31}P nmr, δ −20.5 ppm (heptet, J_{H-P} = 10.6 Hz), by ^1H nmr (Table I), by the mass spectrum with a base peak at *m/e* 164, corresponding to the loss of O=P-$(OCH_3)_2$,[3] and by the infrared spectral bands at 1280 (vs) and 1065 cm^{-1} (vs). The ^1H nmr also indicated the presence of a third methoxyl at 3.48 ppm.

---

(1) G. L. Behelfer, J. R. Maloney, and W. E. Krueger, Abstracts, 163rd National Meeting of the American Chemical Society, Boston, Mass., April 1972, ORGN-157.

(2) The determination of yield of methylnitrite was complicated by the fact that nitrites react with phosphites: J. H. Boyer and J. D. Woodyard, *J. Org. Chem.*, **33**, 3329 (1968).

(3) J. L. Occolowitz and J. M. Swan, *Aust. J. Chem.*, **19**, 1187 (1966).

TABLE I

PMR CHEMICAL SHIFTS

Compd	$COCH_3$	$POCH_3$	$-CH{=}NOH$	OH
2	3.48	3.55, 3.75	7.71	10.8
3	3.28	3.53, 3.75		11.2
4	3.45	3.68, 3.74		

Compound **2** reacted smoothly with refluxing acetic anhydride in a reaction typical of aldoximes to give the nitrile **3** in 89% yield. Further evidence for the oxime function in **3** was provided by the ^1H nmr, δ 10.8 (s, exchangeable) and 7.71 ppm (s), and by the infrared spectrum, ν 3550 (w) and 3220 cm^{-1} (s, broad).

The oxidation of **2** with cold, dilute, neutral potassium permanganate gave an acidic product, **4**, whose elemental analyses were consistent with an empirical formula of $C_{11}H_{15}O_6P$. This was in good agreement with the mass spectrum, which showed a molecular ion at M^+ 274. That carbon was not lost in this reaction and that the product was an acid indicated that the third methoxyl was on the carbon α to the phenyl group. This is also in agreement with the observed singlet for the aldoximino proton of **2** at 7.71 ppm. These data are consistent only with 2-dimethoxyphosphinyl-2-methoxy-2-phenylacetaldehyde oxime as the structure of **2**.

The mechanistic implications of these results currently are being investigated.

Experimental Section[4]

2-Dimethoxyphosphinyl-2-methoxy-2-phenylacetaldehyde Oxime (2).—A solution of 30 g (0.2 mol) of β-nitrostyrene (**1**) in 300 ml of *tert*-butyl alcohol was placed in a three-neck flask equipped with a condenser, pressure-equalizing dropping funnel, and thermometer and 62 g (0.5 mol) of trimethyl phosphite was run in. An initial cooling of 4° was observed followed by a slow increase in temperature to a maximum of 65–75° usually within 20 min. The reaction was accompanied by a slight darkening and a barely discernible gas evolution at higher temperatures. After 3 hr the solvent was removed by rotary evaporation, the residue was cooled and seeded, and the walls of the vessel were scratched. Slow crystallization from the red oil began immediately. After standing overnight the crystals were filtered, washed twice with 20 ml of toluene, and recrystallized from 1,2-dimethoxymethane to give 16.63 g of white, crystalline **2**, mp 134–136°. A second crop from the reaction mixture treated in the same way gave an additional 1.92 g for a total yield of 34%: mass spectrum *m/e* (rel intensity) M^+ 273 (0.5), 243 (18), 164 (100), 132 (83), 105 (37), 77 (42); ^1H nmr ($CDCl_3$) δ 3.47 and 3.48 (pair of singlets, 3, $COCH_3$), 3.55 (d, 3, J_{HP} = 10.6 Hz, $POCH_3$), 3.75 (d, 3, J_{HP} = 10.6 Hz, $POCH_3$),[5] *ca.* 7.40 (m, 5, C_6H_5-), 7.71 ppm (s, 1, $-CH{=}N$), 10.8 (s, 1, OH); ^{31}P nmr ($CHCl_3$) δ -20.5 ppm [heptet, J_{HP} = 10.6 Hz, $P(O)(OCH_3)_2$]; ir ($CHCl_3$) 3550 (w) and 3220 (s, br, OH), 1280 (vs, P=O), 1065 cm^{-1} (vs, POC). *Anal.* Calcd for $C_{11}H_{16}NO_5P$: C, 48.35; H, 5.90; N, 5.13; P, 11.33. Found: C, 48.20; H, 5.91; N, 5.15; P, 11.83.

The red oil that remained was not distillable at pressures of 0.25 mm and temperatures of 180–200°.

The reaction also produced an undetermined amount of a colorless gas which was trapped with a Dry Ice–acetone cold finger distillation head placed at the top of the water-jacketed condenser: nmr (CCl_4) δ 3.98 ppm (s, CH_3ONO); ir (CCl_4) 1665 (s) and 1610 cm^{-1} (s, $-ONO$). These spectra were identical with those of an authentic sample of methyl nitrite prepared by reaction of methyl iodide with sodium nitrite in dimethylformamide.

2-Dimethoxyphosphinyl-2-methoxy-2-phenylacetonitrile (3).—The white solid **2**, 5.4 g (0.02 mol), and 20 ml of acetic anhydride were placed in a round-bottom flask with condenser and heated at reflux for 8 hr. The volatile materials were removed at aspirator pressure and the residue was distilled to give 4.54 g (89%) of a water-white liquid, bp 140–144° (0.7 mm). Redistillation gave an analytical sample: bp 133–135° (0.25 mm); ir (CCl_4) 2250 cm^{-1} (vw, $C{\equiv}N$);[6] nmr (CCl_4) δ 3.28 (s, 3, $COCH_3$), 3.53 (d, 3, J_{HP} = 10.5 Hz, $POCH_3$), 3.75 (d, 3, J_{HP} = 10.5 Hz, $POCH_3$),[5] 7.41 ppm (m, 5, C_6H_5); mass spectrum *m/e* (rel intensity) 255 (0.5), 146 (100), 109 (8), 105 (49), 77 (12). *Anal.* Calcd for $C_{11}H_{14}NO_4P$: C, 51.72; H, 5.53. Found: C, 51.59; H, 5.53.

2-Dimethoxyphosphinyl-2-methoxy-2-phenylacetic Acid (4).—A solution of 2.73 g (0.01 mol) of **2** in 150 ml of water, which was prepared by warming the water until the solid **2** just dissolved, was added to a solution of 1.58 g of $KMnO_4$ in 150 ml of H_2O in such a way that the temperature did not go above 35°. After 0.5 hr the mixture was filtered and the water was removed under vacuum. The solid–oil mixture that resulted was taken up in $CHCl_3$ and extracted three times with 20 ml of 10% K_2CO_3 solution. The combined water layers were extracted once with 15 ml of $CHCl_3$ and neutralized with excess HCl. The turbid mixture was extracted three times with 20 ml of $CHCl_3$ and the combined organic layers were dried over $MgSO_4$ and evaporated to give 1.44 g of a yellow oil Trituration in benzene gave a white solid which was collected by filtration Recrystallization from toluene gave 0.86 g (31%) of **4** as a white solid: mp 148–150°; mass spectrum *m/e* (rel intensity) 274 (0.5), 230 (18), 215 (15), 165 (61), 121 (94), 105 (100), 77 (61); ir 1750 (s, C=O), 1240 (s, P=O), 1060 cm^{-1} (s, POC); nmr ($CDCl_3$) δ 3.45 (s, 3, $COCH_3$), 3.68 (d, 3, J = 10.5 Hz, $POCH_3$), 3.74 (d, 3, J = 10.5 Hz, $POCH_3$),[5] *ca.* 7.5 (m, 5, C_6H_5), 11.2 ppm (s, 1, CO_2H). *Anal.* Calcd for $C_{11}H_{15}O_6P$: C, 48.18; H, 5.51; P, 11.29. Found: C, 48.31; H, 5.22; P, 11.16.

Acknowledgments.—We acknowledge the support of donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Research Foundation of the State University of New York for their partial support of this research.

Registry No.—**1**, 102-96-5; **2**, 42151-03-1; **3**, 42151-04-2; **4**, 42151-05-3.

---

(4) Infrared spectra were determined on a Perkin-Elmer Model 221G spectrophotometer, nmr spectra on a Hitachi Perkin-Elmer R-20B, and mass spectra on a Du Pont Model 21-491 gc–mass spectrometer.

(5) The nonequivalence of methoxyl groups is expected of phosphinyl groups attached to a carbon bearing three different substituents and further supports structures **2**, **3**, and **4**: R. H. Bible, "Interpretation of NMR Spectra," Plenum Press, New York, N. Y., 1965, p 75; J. H. Boyer and R. Selvarajan, *J. Org. Chem.*, **35**, 1229 (1970).

(6) The nitrile infrared band may disappear altogether when attached to a carbon bearing an oxygen: L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Wiley, New York, N. Y., 1966, p 266.

Convenient, High Yield Conversion of Androst-5-ene-3β,17β-diol to Dehydroisoandrosterone

HIROSHI HOSODA, DAVID K. FUKUSHIMA, AND JACK FISHMAN*

Institute for Steroid Research,
Montefiore Hospital and Medical Center, Bronx, New York 10467

Received July 16, 1973

In connection with the investigation of the mechanism of steroid biotransformations we required dehydroisoandrosterone labeled with tritium in specific locations and orientation. To prepare these substrates with adequate specific activities, a convenient and high yield method of converting androst-5-ene-3β,17β-diol which is readily obtainable from androstenedione or testosterone to dehydroisoandrosterone was required. Since direct selective oxidation of the