7-(β-D-Ribofuranosyl)pyrrolo[2,3-*d*]-4-pyrimidone-5-carboxamidine (10).—7-(β-D-Ribofuranosyl)pyrrolo[2,3-*d*]-4-pyrimidone-5-carboxamidoxime (**9**, 500 mg) was dissolved in 50 ml of water containing 8 drops of 25% ammonium hydroxide. To this solution was added 2.5 g of commercial Raney nickel, and the reaction mixture was heated at reflux temperature with continuous stirring for 5 hr. The catalyst was removed by filtration through a Celite pad and the Celite pad was washed with four 10-ml portions of boiling water. The product, which had separated from solution when the combined washings and filtrate were cooled to room temperature, was collected by filtration. The product was recrystallized from water to yield 100 mg (21%) of **10**, mp 272° dec.

Anal. Calcd for $C_{12}H_{15}N_5O_5$: C, 46.70; H, 4.90; N, 22.60. Found: C, 46.40; H, 4.93; N, 22.52.

Ethyl 7-(β-D-ribofuranosyl)pyrrolo[2,3-*d*]-4-pyrimidone-5-formimidate hydrochloride (16).—5-Cyano-7-(β-D-ribofuranosyl)pyrrolo[2,3-*d*]-4-pyrimidone (**13**, 500 mg) was slurried in 50 ml of ethanol and dry hydrogen chloride gas was bubbled through this mixture for 0.5 hr with stirring while the reaction mixture was maintained at room temperature. The resulting slurry was evaporated to dryness, ethanol was added, and the slurry was again evaporated to dryness, this process being repeated several times to remove all excess hydrogen chloride. The solid was recrystallized from ethanol and dried for 2 hr *in vacuo* over P_2O_5 to yield 320 mg (55%) of pure product, mp 158–160° (foams). There was no peak observed in the 2250-cm^{-1} region of the infrared spectrum.

Anal. Calcd for $C_{14}H_{18}N_4O_6 \cdot HCl$: C, 45.00; H, 4.84; N, 14.95. Found: C, 45.30; H, 5.01; N, 15.00.

7-(β-D-ribofuranosyl)pyrrolo[2,3-*d*]-4-pyrimidone-5-carboxamidrazone (14).—Ethyl 7-(β-D-ribofuranosyl)pyrrolo[2,3-*d*]-4-pyrimidone-5-formimidate hydrochloride (**16**, 100 mg) was dissolved in 12 ml of ethanol and 0.02 ml of anhydrous hydrazine was then added. A precipitate began to separate from solution after 0.5 hr and the solution was stirred for a total of 5 hr at room temperature. The solvent was removed *in vacuo* and the residue was crystallized from ethanol–water to yield 50 mg (52%), mp 266–274° dec. Recrystallization of this crystalline material from water yielded a small amount of pure compound, which was dried *in vacuo* over P_2O_5 for analysis; mp 264–266°.

Anal. Calcd for $C_{12}H_{16}H_6O_5 \cdot H_2O$: C, 42.20; H, 5.30; N, 24.60. Found: C, 42.75; H, 5.27; N, 24.55.

Registry No.—**1**, 18417-89-5; **2** dihydrochloride, 22242-87-1; **3** hydrochloride, 22242-88-2; **4**, 22242-89-3; **6**, 22242-90-6; **7**, 22242-91-7; **9**, 22242-92-8; **10**, 22242-93-9; **11**, 22242-94-0; **12**, 22242-95-1; **13**, 22242-96-2; **14**, 22242-97-3; **16** hydrochloride, 22242-98-4.

Notes

Synthesis and Cleavage of Phospholane Oxides

B. R. EZZELL[1a] AND LEON D. FREEDMAN[1b]

Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27607

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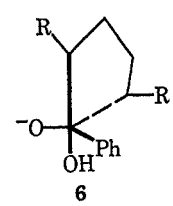
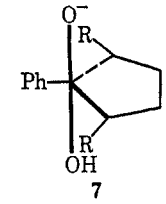
In a recent paper[2] we reported that the heterocyclic ring of the dibenzophosphole 5-oxide system exhibits an unexpected instability toward alkaline cleavage. In contrast to these results, we have now found that the cleavage of two derivatives of 1-phenylphospholane 1-oxide with fused sodium hydroxide obeys the general rule, *viz.*, that the group that is preferentially cleaved is the one capable of forming the more stable carbanion.[3] Hence the phospholane ring *per se* appears to have no decisive influence on which carbon–phosphorus bond is cleaved.

The compounds used in the present study were prepared as shown in Scheme I. It should be noted that Campbell and coworkers[4] reported the formation of **3** under essentially the same conditions that we employed for the preparation of **2**. They reported a melting point of 205–207° for **3**. This value does not agree with our melting point for either **2** (178–180°) or **3** (151–153°). Both of our hydrogenation reactions consumed the calculated amount of hydrogen for reduction to the structures shown in Scheme I. In addition, we obtained elemental analyses and nmr spectra consistent with structures **2** and **3**. That the phenyl group of **2** was attached to phosphorus was unequivocally shown by the fact that fusion with sodium hydroxide (discussed below) produced benzene.

As indicated in Scheme II, fusion of the phospholane oxides **2** and **3** with sodium hydroxide yielded 1-hydroxy-2,5-dicyclohexylphospholane 1-oxide (**4**) and (1,4-diphenylbutyl)phenylphosphinic acid (**5**), respectively. Thus, in both reactions, cleavage occurred so as to form the more stable carbanion. Two structures (**6** and **7**) should be considered for the trigonal-bipyramidal intermediate formed during the reaction of the phospholane oxides with sodium hydroxide.[5] There is less ring strain in **6**, since the heterocyclic ring spans one equatorial and one apical position.[6] However, as we have previously suggested,[2] the formation of intermediates comparable to **6** is probably inhibited because



6



7

(1) (a) Taken from the Ph.D. Dissertation of B. R. E., North Carolina State University, Raleigh, N. C., 1969; (b) to whom inquiries should be addressed.

(2) B. R. Ezzell and L. D. Freedman, *J. Org. Chem.*, **34**, 1777 (1969).

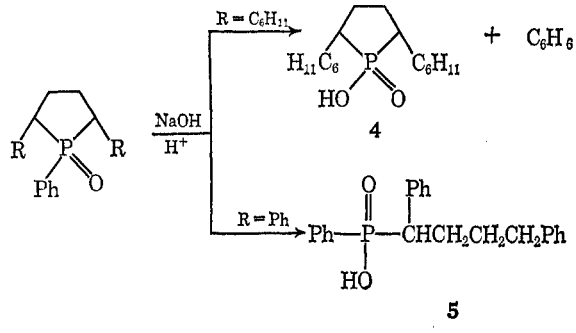
(3) L. Horner, H. Hoffman, and H. G. Wippel, *Chem. Ber.*, **91**, 64 (1958).

(4) I. G. M. Campbell, R. C. Cookson, M. B. Hocking, and A. N. Hughes, *J. Chem. Soc.*, 2184 (1965).

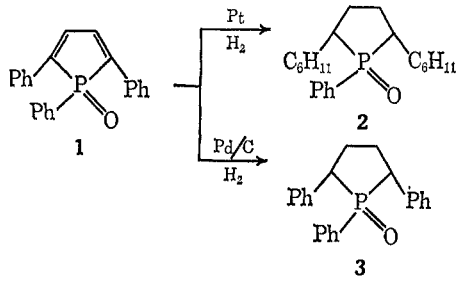
(5) A third possible intermediate having the ring in diequatorial positions and the oxygens in equatorial and apical positions is unlikely for reasons previously discussed.[2]

(6) F. H. Westheimer, *Accounts Chem. Res.*, **1**, 70 (1968).

SCHEME I



SCHEME II



of serious coulombic repulsion between the approaching hydroxide ion and the oxide oxygen atom. Although there is some increase in ring strain in going to intermediate **7**, its formation is favored by minimum coulombic repulsion and by the fact that the electronegative oxygen atoms in **7** occupy apical positions.[6]

It seems reasonable to conclude that the reaction of tertiary phosphine oxides with fused sodium hydroxide normally proceeds through trigonal-bipyramidal intermediates in which oxygen atoms occupy the apical positions. Exceptions to this rule must occur in the case of those heterocyclic compounds in which there would be a large increase in ring strain in going to an intermediate in which the phosphorus atom must span two equatorial positions. In general, however, cleavage probably takes place at an equatorial position of a trigonal-bipyramidal intermediate. By contrast, the alkaline cleavage of quaternary phosphonium salts normally involves the loss of a carbanion from an apical position of a trigonal-bipyramidal intermediate.[2]

Experimental Section[7]

1,2,5-Triphenylphosphole 1-Oxide (1).—1,2,5-Triphenylphosphole[4] (12.0 g, 0.039 mol) was dissolved in tetrahydrofuran (150 ml) and the stirred solution was treated dropwise with 30% hydrogen peroxide (15 ml). The phosphine oxide began crystallizing during the addition. After the addition, the solution was evaporated to 50 ml, cooled, and filtered: yield 11.4 g (91%); mp 234–237° (lit.[4] mp 237–239°).

1-Phenyl-2,5-dicyclohexylphospholane 1-Oxide (2).—1,2,5-Triphenylphosphole 1-oxide (3.4 g, 0.010 mol) was dissolved in a 2:1 mixture of acetic acid–ethyl acetate. Platinum oxide (2 g) was added, and the phosphole oxide was reduced at room temperature and 4 atm in a Parr hydrogenation apparatus. After 2 hr, the uptake of hydrogen was equivalent to eight double bonds. The catalyst was separated by filtration, and the solvent was evaporated. The product was obtained by recrystallization of the residue from ethyl ether–petroleum ether: yield 2.6 g (72%); mp 178–180°; nmr τ 7.5–9.0 (m, 28, aliphatic H) and 2.0–2.7 (m, 5, aromatic H).

Anal. Calcd for $C_{22}H_{33}OP$: C, 76.71; H, 9.66; P, 8.99. Found: C, 77.00; H, 9.46; P, 9.42.

1,2,5-Triphenylphospholane 1-Oxide (3).—1,2,5-Triphenylphosphole 1-oxide (5.0 g, 0.015 mol) was dissolved in a 2:1 acetic acid–ethyl acetate mixture. Palladium (0.75 g of 10% palladium on carbon) was added, and the compound was reduced at room temperature and 4 atm. After 3 hr, the uptake of hydrogen was equivalent to two double bonds. The catalyst was separated, and the solvent was evaporated. The residue was recrystallized from carbon tetrachloride: yield 4.05 g (80%); mp 151–153° (lit.[4] mp 205–207°); nmr τ 7.1–7.6 (m, 4, CH_2CH_2), 6.02 (d, J_{PH} = 22.5 Hz, further split into triplets, J = 9.0 Hz, 2, HCPCH), and 2.7–3.1 (m, 15, aromatic H).

Anal. Calcd for $C_{22}H_{21}OP$: C, 79.50; H, 6.37; P, 9.32. Found: C, 79.40; H, 6.30; P, 9.28.

Cleavage of 1-Phenyl-2,5-dicyclohexylphospholane 1-Oxide (2).—The phosphine oxide **2** (2.7 g, 0.0079 mol) was thoroughly mixed with finely powdered sodium hydroxide (0.05 mol) in a 25-ml pear-shaped flask fitted with a condenser. The flask was slowly heated to 300° and maintained between 300 and 310° for 1.5 hr. About 0.7 ml of benzene (identified by nmr and ir), essentially the calculated amount for exclusive phenyl cleavage, distilled during this time. The contents of the flask were dissolved in water, treated with charcoal, and acidified to give 1-hydroxy-2,5-dicyclohexylphospholane 1-oxide (**4**): yield 1.75 g (79%); mp 272–276° after recrystallization from glacial acetic acid. The ir did not show any aromatic CH stretches, but had aliphatic CH stretches at 2850 and 2920 cm^{-1} and a wide band centered at 950 cm^{-1}. The nmr spectrum showed a wide multiplet at τ 7.6–9.1.

Anal. Calcd for $C_{16}H_{29}O_2P$: C, 67.58; H, 10.28; P, 10.89. Found: C, 67.57; H, 10.31; P, 11.00.

Cleavage of 1,2,5-Triphenylphospholane 1-Oxide (3).—This phosphine oxide (3.0 g, 0.0090 mol) was cleaved with sodium hydroxide (1.5 g) at 300° for 1.5 hr by the procedure described for 1-phenyl-2,5-dicyclohexylphospholane 1-oxide. No hydrocarbon distilled during the reaction. The usual isolation procedure gave (1,4-diphenylbutyl)phenylphosphinic acid (**5**): yield 2.8 g (89%); mp 143–147° after recrystallization from ethanol; nmr τ 8.64 (t, J = 7.0 Hz, 2, $PCCH_2$), 8.08 (m, 2, CCH_2C), 7.65 (m, 2, CH_2Ph), 7.10 (t, with further splitting, J_{PH} = 14.0 Hz, 1, PCH), and 2.5–3.2 (m, 15, aromatic H).

Anal. Calcd for $C_{22}H_{22}O_2P$: C, 75.41; H, 6.62; P, 8.84. Found: C, 75.29; H, 6.73; P, 8.85.

Registry No.—**2**, 22137-71-9; **3**, 1045-11-0; **4**, 22155-43-7; **5**, 22137-73-1.

(7) Melting points were taken with a Mel-Temp capillary melting point apparatus and are uncorrected. Infrared spectra were taken on a Perkin-Elmer Model 521 spectrophotometer. Nmr spectra were taken with either a Varian HA-100 or Varian T-60 instrument; deuteriochloroform was used as a solvent with tetramethylsilane as an internal standard. Elemental analyses were performed by Galbraith Laboratories.

Leguminosae Alkaloids. VII. The Synthesis of (±)-Lamprolobine[1a-c]

STANLEY I. GOLDBERG AND ALAN H. LIPKIN

Department of Chemistry, The University of South Carolina, Columbia, South Carolina 29208

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The alkaloid lamprolobine, isolated from *Lamprolobium fruticosum*, was recently assigned the structure (−)-(1*R*,5*R*,10*R*)-1-(glutarimidomethyl)quinolizidine (**I**) on the basis of evidence obtained from a degradative study.[2] Lamprolobine represents the first natural

(1) (a) We thank the National Institute of Mental Health for the grant under which this work was supported; (b) we gratefully acknowledge the departmental grant awarded by the National Science Foundation which contributed toward the purchase of the mass spectrometer used in this work; (c) we wish to express our warmest thanks to Dr. J. A. Lamberton of CSIRO, Australia, for his courtesy in providing a generous sample of (−)-lamprolobine.

(2) N. K. Hart, S. R. Johns, and J. A. Lamberton, *Aust. J. Chem.*, **21**, 1619 (1968).