Jr., *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1), 146 (1969); *Chem. Abstr.*, **70**, 106077*r* (1969).
(11) E. W. Heffern, Ph.D. Thesis, Illinois Institute of Technology, Chicago, Ill., 1969.
(12) W. S. Wadsworth, Jr., and W. D. Emmons, *J. Amer. Chem. Soc.*, **83**, 1737 (1961).
(13) J. M. Birchall, F. L. Bowden, R. N. Haszeldine, and A. B. P. Lever, *J. Chem. Soc.*, 747 (1967).
(14) N. P. Buu-Hoi and G. Saint-Ruf, *Bull. Soc. Chim. Fr.*, 606 (1968).
(15) R. Filler and E. W. Choe, submitted for publication.
(16) R. Filler, Y. S. Rao, A. Biezais, F. N. Miller, and V. Beaucaire, *J. Org. Chem.*, **35**, 930 (1970).
(17) F. N. Miller, Ph.D. Thesis, Illinois Institute of Technology, Chicago, Ill., 1967.

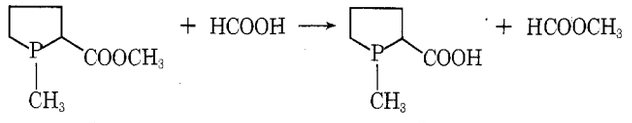
Cleavage by Acid of the Phosphorus–Carbon Bond in Cyclic Phosphines Containing a β-Carbonyl Group[1]

Louis D. Quin* and Charles E. Roser

Department of Chemistry, Paul M. Gross Chemical Laboratory, Duke University, Durham, North Carolina 27706

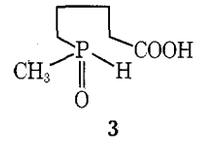
Received July 8, 1974

The C–P bond of simple phosphines is known to withstand the conditions of the common organic reactions. However, we have found that the bond is rendered sensitive to cleavage by an acidic medium when a β-carbonyl group is present. This reaction was encountered in an attempt to effect the conversion of methyl 1-methyl-2-phospholanecarboxylate[2] (1) to the acid (2) by HCl-catalyzed transesterification with formic acid[3] (91%). The crystalline



1 2

solid that was obtained in 71% yield had properties quite unlike those expected for **2**. Through a combination of spectral techniques, it was established to have the ring-opened structure **3**.

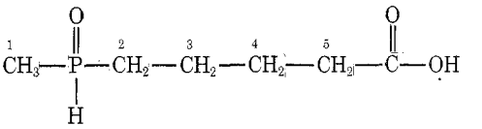


3

The product, which by analysis differed from the expected structure **2** by the elements of H_2O, had infrared spectral bands for a strongly hydrogen-bonded carboxylic acid group, showing that the expected transesterification had occurred. However, there were also P–H (2375 cm^{-1}) and P=O (1100 cm^{-1}) stretching bands, and this suggested the presence of phosphorus in the secondary phosphine oxide function. The P–H bond was also apparent in the ^1H nmr spectrum; a peak appeared at 9.98 ppm in H_2O that was removed on running the sample in D_2O. This proton had been coupled with the P–CH_3 group, for this latter signal, which in H_2O was a doublet of doublets (J_{PCH} = 14, J_{HPCH} = 2 Hz), lost the smaller coupling after D exchange. The peak at 9.98 ppm is half of the P–H signal; the other half is obscured by the H_2O signal. However, in $CDCl_3$ both halves were visible, with δ 7.62 and J_{PH} = 476 Hz. The shift and coupling constant are in line with those known for other secondary phosphine oxides (*e.g.*, for Me_2PHO,[4] δ 7.5, J_{PH} = 490; for Et_2PHO,[4] δ 7.2, J_{PH} = 468; for 3,4-dimethyl-3-phospholene oxide (**4**), which was available from previous work,[5] δ 7.97, J_{PH} = 490 Hz).

The proton-decoupled ^{31}P nmr signal (δ −31.8 in $CHCl_3$, −38.2 in H_2O) was also in the region expected for secondary phosphine oxides (*e.g.*, for Et_2PHO,[4] δ −41.0 and −47.7; for the phospholene oxide **4**, δ −39.8 and −44.4). Replacement of the proton with deuterium introduces a valuable structure diagnostic effect; the phosphorus singlet is split to a 1:1:1 triplet with a characteristic coupling (for **3**, J = 73 Hz; other secondary phosphine oxides gave similar values [4]).

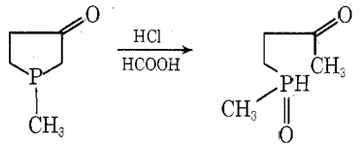
The ^{13}C nmr spectrum also proved the secondary phosphine oxide structure. Carbons attached to phosphoryl groups have large (60–100 Hz) coupling constants,[6] and are readily recognized. For **3**, there would be two such signals of roughly equal intensity and these were observed at δ 13.0 with J_{PC} = 64 Hz (C-1) and δ 29.0 with J_{PC} = 65 Hz (C-2). The complete assignment is shown below.



δ:	13.0	29.0	21.2	26.1	34.3	179.0
J_{PC}:	64	65	<2	10	s	s

C-5 is easily recognized since it should be quite similar in position to the α-carbon of pentanoic acid (δ 34.5).[7] The assignment of C-3 and C-4 rests first on a coupling effect with ^{31}P; it is known that in aliphatic tertiary phosphine sulfides and oxides, $^3J_{PC}$ exceeds $^2J_{PC}$,[8] and since this should prevail also in secondary oxides, C-4 is the signal with J_{PC} = 10 Hz. Chemical shift relations support this assignment. Thus, C-4 should have a shift much like that of the β-carbon of pentanoic acid, since phosphorus groups are known to exert only a slight effect on a carbon in this position.[8] The C-4 shift of 26.1 ppm corresponds well to that of the β carbon of pentanoic acid (δ 25.2).[7] C-3 is upfield of C-4 because it undergoes γ-shielding effects[8] with both CH_3 and O on phosphorus.

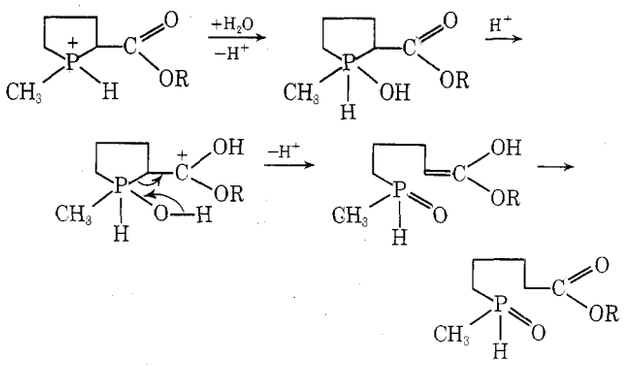
The generality of the cleavage process was tested with another β-carbonyl phosphine, compound **5**, which was available from previous work.[9] The HCl–formic acid treatment should produce structure **6**, and the product obtained had spectral properties (see Experimental Section) that confirmed this expectation. The product was a noncrystal-



5 6

lizing oil, and complete characterization was not possible. There is no doubt, however, that the ring cleavage occurred, and that secondary phosphine oxide **6** was formed.

The mechanism of the cleavage of these β-carbonylphosphines presumably involves attack of water on the proton-



ated phosphine. A possible sequence of events to account for the product is shown above. The transesterification may occur before or after the ring cleavage.

Experimental Section

General. Reactions of phosphines were conducted under nitrogen. Mp values are corrected. Proton nmr spectra were taken with JEOL MH-100 or Varian T-60 spectrometers. Proton-decoupled ^{31}P nmr spectra were taken on a Bruker HFX-10 system at 36.43 MHz; shifts are relative to external 85% H_3PO_4. The proton-decoupled ^{13}C nmr spectrum was obtained by the Fourier transform technique on the Bruker spectrometer at 22.62 MHz utilizing C_6F_6 as external heteronuclear lock in a 3-mm coaxial capillary. Analyses were performed by MHW Laboratories, Garden City, Mich.

Synthesis of Methyl(4-carboxybutyl)phosphine Oxide (3) from Methyl 1-Methylphospholane-2-carboxylate (1). To 30 ml of deoxygenated 91% formic acid was added 0.40 g (0.0025 mol) of a 60:40 cis:trans mixture of 1.[2] Dry hydrogen chloride generated from sodium chloride and concentrated sulfuric acid was bubbled for 10 min through the resulting solution, which was then refluxed for 24 hr under nitrogen. The reflux condenser was equipped with a take-off valve, and a total of 10 ml of distillate containing the methyl formate produced was drawn off during the reaction period. After the reflux period was complete, the formic acid was distilled off at water-aspirator pressure. Water was added and the distillation repeated to remove remaining traces of formic acid. A light brown oil remained which solidified upon drying overnight at high vacuum. This solid was recrystallized from chloroform–petroleum ether and yielded 0.29 g (71%) of white crystalline **3**, mp 87–88°.

The ^1H nmr spectrum (external TMS) gave the following signals: in H_2O, δ 2.15 (d of d, *P*-CH_3, $^2J_{PH}$ = 14 Hz, $^3J_{HH}$ = 2 Hz), 1.9–2.7 and 2.8–3.2 (multiplets, CH_2), δ 9.98 (half of doublet of sextets with other half under H_2O absorption, *P*-H, $^3J_{HH}$ = 2 Hz); in D_2O, δ 2.15 (d, *P*-CH_3, $^2J_{PH}$ = 14 Hz), 9.98 was absent, rest unchanged; in $CDCl_3$ δ 1.9–2.7 and 2.7–3.3 (two broad peaks, indistinct *P*-CH_3 and CH_2), δ 7.62 (d of broad peaks, *P*-H, $^1J_{PH}$ = 476 Hz), 10.31 (broad s, COOH). The ^{31}P nmr had signals at δ −38.2 in H_2O, −37.8 in D_2O (t, $^1J_{PD}$ = 73 Hz), and −31.8 in $CHCl_3$. The ^{13}C nmr (H_2O, *p*-dioxane as internal reference, δ^{TMS} = 67.8 ppm) is described in the discussion. The infrared spectrum (KBr disk) contained absorptions at 2550, 2900, and 1925 for hydrogen bonded OH stretch, ν_{PH} 2375, $\nu_{C=O}$ 1700, $\nu_{P=O}$ 1110 cm^{-1}.

Anal. Calcd for $C_6H_{13}O_3P$: C, 43.91; H, 7.99; P, 18.87. Found: C, 43.60; H, 7.93; P, 18.56.

Cleavage of 1-Methyl-3-phospholanone (5). By the same procedure as above, 0.9 g (0.0073 mol) of **5**[9] was treated with formic acid–HCl. A light green oil was obtained after removal of all the formic acid. Addition of chloroform dissolved most of the oil leaving a small amount of green residue. The chloroform was removed by rotary evaporation, which yielded 0.52 g (51%) of **6** as a thick, almost colorless oil. All attempts to crystallize the oil proved unsuccessful.

The ^1H nmr spectrum (H_2O, external TMS) gave the following signals: in H_2O, δ 2.03 (d of d, *P*-CH_3, $^2J_{PH}$ = 14 Hz, $^3J_{HH}$ = 4 Hz), 2.4–3.0 (m, CH_2), 2.61 (s, CH_3CO), 10.02 (broad signal with indistinct additional splitting, half of *P*-H doublet); in D_2O, δ 2.02 (d, *P*-CH_3, $^2J_{PH}$ = 14 Hz), 10.02 was absent, rest unchanged; in $CDCl_3$, δ 2.16 (broad d, *P*-CH_3, $^2J_{PH}$ = 13–14 Hz), 2.4–3.0 (m, CH_2), 2.75 (s, CH_3CO), 7.72 (broad d, *P*-H, $^1J_{PH}$ = 474 Hz). The ^{31}P nmr signal was at δ −38.2 in H_2O, −37.0 in D_2O (t, $^1J_{PD}$ = 76 Hz) and −27.5 in $CDCl_3$. The ir spectrum (neat) had $\nu_{C=O}$ 1720 and $\nu_{P=O}$ 1155 cm^{-1}.

Spectra of 3,4-Dimethyl-3-phospholene 1-Oxide (4). This compound was prepared as previously reported.[5] The ^1H nmr spectrum (external TMS) had the following signals: in H_2O, δ 2.22 (s, *C*-CH_3), 2.78–3.50 (m, CH_2), 10.35 (broad, half of *P*-H doublet, removed with D_2O); in $CDCl_3$ the PH signal occurred at δ 7.97 (J_{PH} = 490 Hz). The ^{31}P nmr signal was at δ −44.4 in H_2O, −44.1 in D_2O (t, $^1J_{PD}$ = 76 Hz), and −39.8 in $CDCl_3$.

Registry No.—*cis*-**1**, 52500-00-2; *trans*-**1**, 52500-01-3; **3**, 52571-12-7; **4**, 52500-02-4; **5**, 49849-35-6; **6**, 52571-13-8.

References and Notes

(1) Supported by Public Health Service Research Grant CA-05507 from the National Cancer Institute. The National Science Foundation provided funds toward the purchase of the Bruker spectrometer (Grant No. GP-10301).
(2) S. G. Borleske and L. D. Quin, *Phosphorus*, in press.
(3) C. E. Rehberg, "Organic Syntheses," Collect. Vol. III, Wiley, New York, N.Y., 1955, p 33.
(4) L. A. Hamilton and P. S. Landis, in "Organic Phosphorus Compounds," Vol. 4, G. M. Kosolapoff and L. Maier, Ed., Wiley-Interscience, New York, N.Y., 1972, p 490.
(5) D. K. Myers and L. D. Quin, *J. Org. Chem.*, **36**, 1290 (1972).
(6) See, for example, G. A. Gray and S. E. Cremer, *J. Org. Chem.*, **37**, 3458, 3470 (1972); J. J. Breen, S. I. Featherman, L. D. Quin, and R. C. Stocks, *Chem. Commun.*, 657 (1972).
(7) R. Hagen and J. D. Roberts, *J. Amer. Chem. Soc.*, **91**, 4504 (1969).
(8) L. D. Quin, M. D. Gordon, and S. O. Lee, *Org. Magn. Resonance*, in press.
(9) L. D. Quin and R. C. Stocks, *J. Org. Chem.*, **39**, 686 (1974).

New Facile Method for Conversion of Oximes to Nitriles. Preparation and Acid-Catalyzed Transformation of Aldehyde Oxime Ortho Esters

Milorad M. Rogić,* Jan F. Van Peppen, Karl P. Klein, and Timothy R. Demmin

Chemical Research Center, Allied Chemical Corporation, Morristown, New Jersey 07960

Received May 12, 1974

We wish to report a new and facile conversion of aldoximes to the corresponding nitriles by an acid-catalyzed reaction of aldoximes and ortho esters (eq 1).

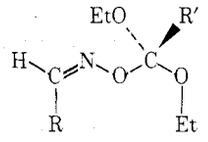
$$RCH{=}NOH + R'C(OEt)_3 \xrightarrow{H^-} RCN + R'COOEt + 2EtOH \quad (1)$$

Heating a mixture of equivalent amounts of an aldoxime and an ortho ester in the presence of a catalytic amount of an acid resulted in formation of the corresponding nitrile, ester, and alcohol. Simple distillation of the ester and the alcohol thus produced (eq 1), followed by vacuum distillation of the residue, afforded the nitrile usually in high yield. The general nature of the reaction is indicated by the results summarized in Table I. The primary product in this transformation is the oxime dialkyl ortho ester[1] which can be easily isolated in high yield by distilling off 1 equiv of the alcohol from an equimolar mixture of the oxime and the ortho ester *in the absence of acid catalysts* (eq 2).

$$RCH{=}NOH + R'C(OEt)_3 \rightleftharpoons RCH{=}NOCR'(OEt)_2 + EtOH \quad (2)$$

For example, distillation of 1 equiv of ethanol from a reaction mixture of equimolar amounts of *n*-butyraldehyde oxime (a mixture of *Z* and *E* isomers in the approximate ratio of 3:2) and triethyl orthoacetate, followed by vacuum distillation, gave a 95% yield of *n*-butyraldehyde oxime diethyl orthoacetate. Similarly, *Z*-benzaldehyde oxime and triethyl orthoformate gave an 86% yield of benzaldehyde oxime diethyl orthoformate. Analysis of these reactions *via* nmr spectroscopy indicated that no oxime isomerization had occurred under the reaction conditions.[3] The formation of oxime dialkyl ortho esters is evidently also a general reaction as indicated in Table II.

The oxime dialkyl ortho esters undergo an acid-catalyzed Beckmann fragmentation reaction providing the corresponding nitrile, ester, and alcohol[5] (eq 3). This reaction



$$\xrightarrow{H^-} RCN + R'COOEt + EtOH \quad (3)$$