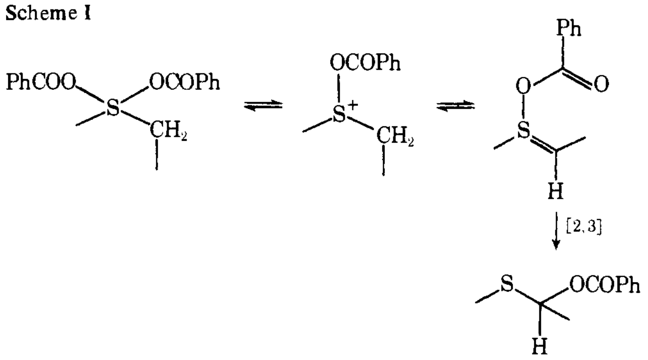
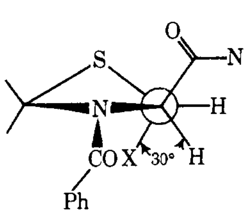
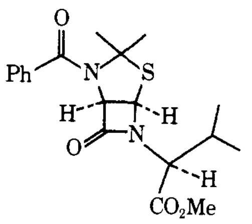
Scheme I



peptide **4** and its derivatives. Since the required oxidation at C3 of the cysteine moiety of **4** necessitated stereospecific removal of one of the C3 hydrogens, rotation around the C2–C3 bond was frozen by use of the known thiazolidine (**5**).[2] Peptide bond formation between **5** and L-valine methyl ester mediated by the reagent EEDQ[3] gave the dipeptide **6**, 58%,[4] mp 147–148°, $[\alpha]^{25}_{D}$ −139.6° (c 1, CH_2Cl_2). Stereospecific functionalization at C3 of the cysteine residue in **6** was readily achieved by refluxing with benzoyl peroxide (4 equiv) in CCl_4 (1.5 hr) to provide benzoate **7**, 55%, mp 193–194°, $[\alpha]^{25}_{D}$ 125.3° (c 1, CH_2Cl_2); NMR δ 5.1 (1 H, s), 6.55 (1 H, s) (C2, C3 hydrogens, J = 0 Hz). The mechanism of this facile and stereospecific functionalization probably involves the sequence of Scheme I, i.e., an initial formation of sulfurane, followed by a [2,3]-sigmatropic rearrangement of the intermediate ylide.[5] The clean stereochemistry results from shielding of the upper face of the thiazolidine ring by the bulky valine residue. Hydrolysis of the benzoate **7** was achieved in aqueous neutral dioxane at 125° (4 hr) providing the unstable alcohol **8**, 56%: mp 35° dec; NMR δ 4.82 (1 H, s), 5.45 (1 H, s) (C2, C3 hydrogens, J = 0 Hz). Mesylation of **8** with methanesulfonyl chloride and pyridine (CH_2Cl_2, 0°) gave directly the chloride **9**, 62%: mp 136–137.5°, $[\alpha]^{25}_{D}$ −265° (c 1, CH_2Cl_2); NMR δ 5.2 (1 H, s), 5.98 (1 H, s) (C2, C3 hydrogens, J = 0 Hz). However this chloride **9** was more easily obtained (95%) by direct treatment of benzoate **7** with hydrogen chloride gas (CH_2Cl_2, 0°). These facile exchange processes which proceed with retention of configuration at C3 of the cysteine moiety presumably involve the cation **10**.[6] The remarkable resistance toward β-elimination in this series requires comment. The coupling constant between hydrogens at C2 and C3 of derivatives **7–9** is 0 Hz. This suggests conformation **11** for all of these compounds, in which the C3–X and C2–H bonds are not coplanar and hence resist concerted eliminations. Ring closure of chloride **9** was readily achieved by treatment with NaH (1.1 equiv) in dichloromethane containing tetra-N-butylammonium iodide (0.1 equiv)[7] at 25°, to yield the β-lactam **12** as an oil (81%): $[\alpha]^{25}_{D}$ −304.5° (c 1, CH_2Cl_2), λ_{max} 1765, 1740 1655 cm^{-1}; NMR δ 5.5 (2 H, AB quartet J = 5.5 Hz) (C2, C3 hydrogens).



11



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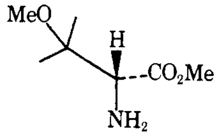

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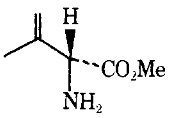

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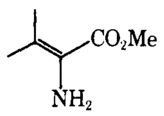

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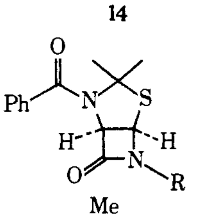
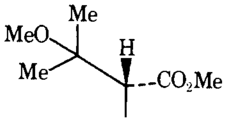
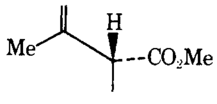


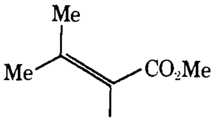
16, R =



17, R =



18, R =



By starting this same sequence with the D-amino acid esters **13** and **14**[8] and also the dehydrovaline ester **15**, it was possible to obtain all three β-lactam containing peptides **16**, **17**, and **18**. The conversion of these latter substances into the naturally occurring β-lactam antibiotics is in progress.[9]

Acknowledgments. We thank the National Science Foundation, the National Institutes of Health, Eli Lilly and Co., Hofmann La Roche, and Merck & Co. for financial support. We also acknowledge helpful discussions with the research staff of Eli Lilly & Co.

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(6) Participation in **10** of the neighboring amide linkage is possible and would also contribute to the high stereospecificity of these reactions.

(7) This is an example of phase transfer catalysis between a solid and liquid phase.

(8) Synthesized in these laboratories by J. E. Baldwin and S. B. Haber, unpublished results.

(9) Professor Y. Kishi has informed us that he has made β-lactams from 2-substituted cysteinyl derivatives by similar base catalyzed closures, personal communication.

(10) Chapin Fellow, 1974–1975.

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Protonation of Phosphorus Trihalides

Sir:

While protonation of phosphorus in $PR_{3-n}(OR')_n$ systems is readily accomplished in strong acid,[1-5] the evidence for the formation of HPX_3^+ cations is limited to a tentative

Table I. ^{31}P NMR Parameters for HPX_3^+ and PX_3

	Z = H$^+$			Z = lone pair		
Compd	$^1J_{PH}$, (Hz)	$^1J_{PF}$, Hz	δ ^{31}P,[a,b] Hz	$^1J_{PF}$, Hz	δ ^{31}P,[b] ppm	$\Delta\delta$ ^{31}P,[g] ppm
ZPF_3	1190.6	1279.3	−16.2 dq	1410[c]	−97.0 q[c]	80.8
ZPF_2Cl	1068.9	1272.8	−66.4 dt	1380[d]	−176 t[d]	109.6
$ZPFCl_2$	979.5	1254.9	−92.0 dd	1326[e]	−224 d[e]	132.0
$ZPCl_3$	911.1		−86.9 d		−219.4 s[f]	132.5
$ZPCl_2Br$	875.6		−61.7 d		−224.6 s[f]	162.9
$ZPClBr_2$	841.2		−31.7 d		−227.4 s[f]	195.7
$ZPBr_3$	809.8		+ 3.0 d		−227.7 s[f]	230.7

[a] Because 85% H_3PO_4 is frozen at −70°, PCl_3 was used as an external standard. All chemical shifts are reported relative to 85% H_3PO_4 for convenience, however. [b] Key: dq = doublet of quartets, dt = doublet of triplets, dd = doublet of doublets, q = quartet, t = triplet, d = doublet, and s = singlet. [c] R. Schmutzler, *Adv. Fluorine Chem.*, 5, 31 (1965). [d] A. Muller, O. Glemser and E. Niecke, *Z. Naturforsch. B*, 21, 732 (1966). [e] A. Muller, E. Niecke, and O. Glemser, *Z. Anorg. Allg. Chem.*, **350**, 256 (1967). [f] These chemical shifts match closely those assigned by E. Fluck, J. R. Van Wazer, and L. C. D. Groenweghe, *J. Am. Chem. Soc.*, 81, 6363 (1959). [g] $\Delta\delta$ ^{31}P is the change in chemical shift upon protonation (δ ^{31}P(HPX_3^+) − δ ^{31}P(PX_3)).

suggestion that HPF_3^+ may undergo rapid proton exchange in a PF_3-HSO_3F solution.[6] In that article a room temperature ^{19}F NMR spectrum was described which consisted of a doublet of doublets ($^1J_{PF}$ = 987 Hz, $^2J_{HPF}$ = 94 Hz) although corroboration of the HPF_3^+ species could not be obtained from ^{1}H or ^{31}P NMR spectral data.

Using a 3:8 volume ratio of $HSO_3F{\cdot}SbF_5$ to liquid SO_2 as a diluent, we have been able to obtain ^{31}P NMR spectral evidence for the formation of $HPF_{3-n}Cl_n^+$ (n = 0–3) and $HPCl_{3-n}Br_n^+$ (n = 1–3) at −70°. The acid to phosphorus ratio was always in the range of five to ten to one. Following a literature method,[7] PF_3, PF_2Cl, and $PFCl_2$ were prepared while PCl_2Br and $PClBr_2$ were obtained as a mixture which included PCl_3 and PBr_3 by refluxing the latter two compounds in a 2:1 mole ratio at 100° for 24 hr and using the fraction which distilled from 98–99° at atmospheric pressure. ^{31}P data (Table I) were collected with a Bruker HX-90 NMR spectrometer operating at 36.44 MHz in the Fourier mode.

That all of the phosphorus trihalides are protonated at phosphorus is shown by the appearance of a doublet with a large coupling constant (800–1200 Hz) corresponding to $^1J_{PH}$ and by the shift of the ^{31}P resonance to higher applied field. The latter observation is consistent with the upfield shifts noted to occur in $PCl_{4-n}Br_n^+$ [8] and OPX_3[9] compared to the corresponding trivalent derivatives.

Figure 1 displays the ^{31}P NMR spectrum of the HPF_3^+ ion which exhibits the expected doublet of quartets. The $^1J_{PH}$ value of 1190.6 Hz for this cation is the largest reported for these nuclei and can be attributed to a strong Fermi contact interaction induced by the high degree of s character in the P–H bond and to the substantial nuclear charge on phosphorus; both effects stemming from the large electronegativity of fluorine. There is a dramatic nearly linear drop in $^1J_{PH}$ with the sum of the halogen electronegativities (Figure 2) which is ascribable to the accompanying decrease in s character of the protonated phosphorus lone pair. The coordination chemical shift ($\Delta\delta$ ^{31}P in Table I) decreases monotonically with increasing $^1J_{PH}$ upon fluorine and chlorine substitution in PCl_3 and PBr_3, respectively.

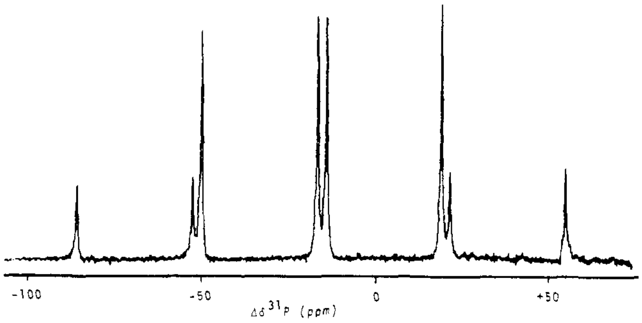

Figure 1. ^{31}P NMR spectrum of HPF_3^+.

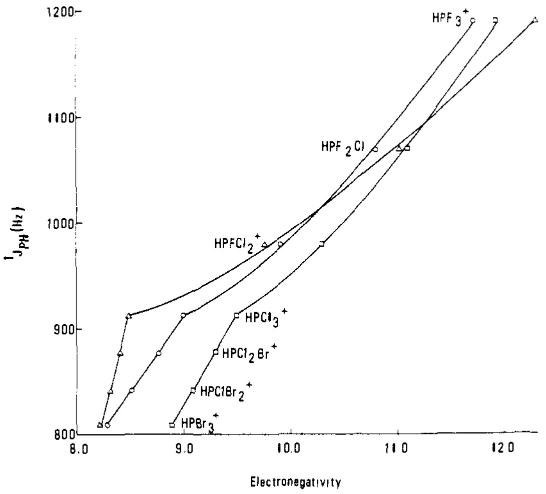

Figure 2. Plot of $^1J_{PH}$ for HPX_3^+ ions vs. the sum of the Allred–Rochow (▼), Mulliken (●), and Pauling (■) halogen electronegativities.

Because $^1J_{PF}$ in both PF_3 and HPF_3^+ exceeds 1250 Hz, it is not likely that the 987 Hz value for this coupling observed by others[6] in the room temperature ^{19}F NMR spectrum is that for HPF_3^+. A sign reversal allowing an intermediate coupling value at the higher temperature (where proton exchange is more likely) is not probable since all PF coupling constants are believed to be negative.[10]

Solvolysis of P–Cl bonds in the $PF_{3-n}Cl_n$ series yielding $PF_{3-n}(SO_3F)_n$ systems is ruled out because (a) the PCl_3-PCl_2Br-$PClBr_2$-PBr_3 mixture would be expected to provide only one (rather than the four observed) protonated species, namely, $HP(SO_3F)_3^+$, owing to the greater lability of bromine, and (b) PCl_3 itself would also have produced $HP(SO_3F)_3^+$.[11] Solvolysis of only the more weakly bound bromines is not as easily dismissed although the following argument strongly militates against such a process. It is reasonable to suppose that the SO_3F group in $P(SO_3F)_3$ is more electronegative than Br in PBr_3 in as much as the P=O stretching frequency in $OP(SO_3F)_3$[12] (which increases from 1261 in $OPBr_3$ to 1290 in $OPCl_3$ to 1415 cm^{-1} in OPF_3[13]) is close to that of OPF_3. The plot in Figure 2 would then be altered in an unexpected way in that the $HPCl_{3-n}(SO_3F)_n^{+\cdot}$ (N = 1–3) series would lie on a *negative* slope which would not intersect the $HPCl_3^+$ point. Further supporting the lack of solvolysis in our experiments is the observation that the ^{31}P spectra changed markedly above ca. −50° with the appearance of new peaks.

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Book Reviews

The Major Ternary Structural Families. By O. MULLER (General Electric Co.) and R. ROY (Pennsylvania State University). Springer-Verlag, New York, N.Y. 1974. ix + 487 pp. $31.20.

This book constitutes Volume 4 of the series "Crystal Chemistry of Nonmetallic Materials". Unfortunately, the earlier volumes of the series have not yet been published, including Volume 1 by Roy and Newnham which is intended to serve as a textbook on crystal chemistry. It is difficult to evaluate the series without seeing Volume 1, but Volume 4 clearly indicates that the approach used is quite "classical" and makes short shrift of modern developments in crystal chemistry.

The ionic model is assumed throughout, and neither objections to the ionic model nor alternative general approaches are treated seriously. In fact, even the latest developments within the ionic model, such as Baur's computer studies of the $(Mg,Fe)_2SiO_4$ polymorphs, are ignored. There is also a problem with regard to the "structure field diagrams", the authors' primary tool for relating structure type to chemical composition for compounds of general formula $A_kB_lX_m$, where A and B are cations and X an anion. In such a diagram the ionic radii of the A cations are plotted against those of the B cations, and the field is then divided according to observed crystal-structure type. The fields thus defined are generally nonoverlapping or slightly overlapping. The first difficulty with this approach as used by Muller and Roy is in their choice of ionic radii. Although the authors state that their ionic radii are similar to those of Shannon and Prewitt, there are, in fact, systematic differences, with common anions being substantially smaller and cations consequently larger than their Shannon and Prewitt values. A discussion of various sets of ionic radii is promised for Volume 1 and may clarify this point. However, the radii presented, when used in conjunction with the conventional radius ratio rules, give incorrect predictions of coordination number; e.g., high-spin Mn^{2+}, with radius ratio of 0.835 with respect to O^{2-}, is predicted to be eight-coordinate in MnO. The failure of the radii to give correct predictions for individual polyhedra must raise doubts about their validity for ternary structures.

The section explaining and justifying the "structure-field" diagrams is quite short and presents an inadequate discussion of the use of the ionic model to calculate internal energies of crystals. The authors ignore the fact, recently discussed in several inorganic chemistry textbooks such as Phillips and Williams and Adams, that the ionic model gives unreliable predictions even on the question of NaCl vs. CsCl structures for the alkali halides. The accuracy of the Born lattice energy equation is certainly less than that assumed by the authors. Also, the empirical validity of the structure-field diagrams does not rest on the ionic model. The success of such diagrams can be explained on the basis first that any bond, no matter what its nature, has an equilibrium internuclear distance. The equilibrium distances within an A-containing polyhedron in a ternary structure will necessarily limit the range of B–X distances present in the possible B-containing polyhedra since the various polyhedra must have elements in common. Therefore, a ternary structure will be stable only if the polyhedra can share structure elements and yet maintain A–X and B–X distances reasonably close to the equilibrium values. The structure field diagrams also show substantial overlap of structure types, in contrast to other methods, such as that of Phillips for A^NB^{8-N} compounds, which effect a clean separation.

The descriptive part of the book is sound, comprehensive, and up-to-date. The material is well organized and will be valuable to researchers in the field. There are lucid and detailed discussions of crystal structure preference for a number of individual compounds and some discussion of the application of structure field diagrams to the prediction of crystal structures for unusual compositions or conditions, an active topic in the mineralogy of the earth's mantle.

In general, the book is sound descriptively and organizationally but is weak in its theoretical presentation. The impression generated is that crystal chemistry is a rather static field, with much new experimental data but little new theory generated since the 1930's.

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Anomalous Photoconductivity. By M. I. KORSUNSKII (Academy of Sciences of the Kazakh SSR). Translated from Russian by E. HARNIK (Hebrew University of Jerusalem). Wiley/Halsted, New York, N.Y. 1973. xi + 166 pp. $23.00.

"Anomalous Photoconductivity" refers to photoconductivity phenomena that can be observed in specially treated, mercury-activated, amorphous selenium. The spectral response of anomalous photoconductivity occurs at longer wavelengths than the strong absorption region of selenium and the spectral region of normal photoconductivity. The magnitude of anomalous conductivity depends only on the spectral composition of the incident light and does not depend upon light intensity. The phenomena can be explained in terms of special impurity centers, or s-centers, that are introduced during the sample preparation procedure.

Reports on anomalous photoconductivity have, to date, appeared primarily in the Russian literature over the past 10–15 years. The monograph is a useful review of the present state of the art regarding anomalous photoconductivity in selenium and brings together material that was formerly distributed throughout the literature. The main features of anomalous photoconductivity are summarized in Chapter 1. This is followed in Chapter 2 by a phenomenological theory which introduces the concept of long-life traps or s-centers (storage centers). Properties of s-centers derived from studies on anomalous photoconductivity are reviewed in Chapter 3. The relationship between anomalous and normal photoconductivity is described in Chapter 4. A detailed description of sample preparation and conditioning procedures is presented in Chapter 5. In the final chapter, possible applications are discussed.

The material is presented in a clear, logical fashion and the standard of the translation is excellent. A few minor errors exist, e.g., on page 2, "importing" should be "imparting". Also, it would have been more helpful if direct references to English translations of Russian journals had been given when cover-to-cover translations exist. These are minor points, however, and such features do not significantly affect the usefulness of the monograph.

The book will be of interest to solid-state physicists, electronic engineers, materials scientists, and chemists with interests in solid-state phenomena.

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