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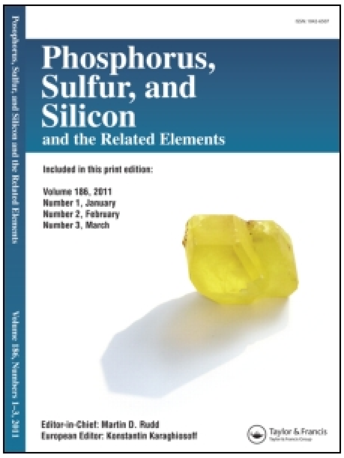

Phosphorus, Sulfur, and Silicon and the Related Elements

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LITERATURE HIGHLIGHTS

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To cite this Article Thyagarajan, B. S. , Barrett, G. C. , Verkade, J. G. and Horner, L.(1983) 'LITERATURE HIGHLIGHTS', Phosphorus, Sulfur, and Silicon and the Related Elements, 16: 3, 373 — 388
To link to this Article: DOI: 10.1080/03086648308080493
URL: http://dx.doi.org/10.1080/03086648308080493

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Phosphorus and Sulfur, 1983, Vol. 16, pp. 373–388
0308-664X/83/1603-0373/$18.50/0

LITERATURE HIGHLIGHTS

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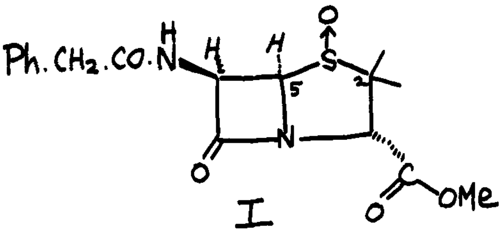
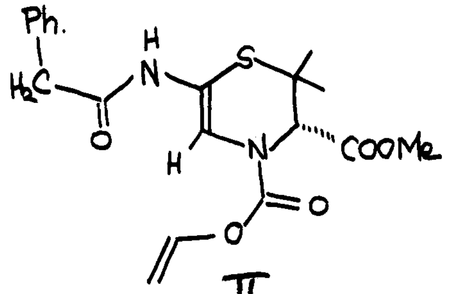
An intriguing and unusual ring cleavage and **rearrangement of a penicillin sulfoxide** is reported with penicillin G—sulfoxide methyl ester (I) which reacts with excess vinyl chloroformate in anhydrous, alcohol-free chloroform solution to give a 56% yield of II.



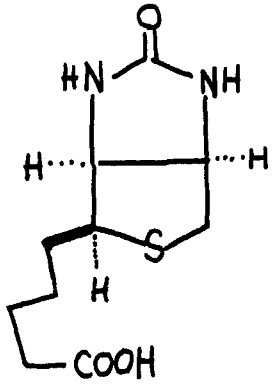
I

The exact mechanism of this cleavage is not yet determined but it is suspected that a cleavage of the C_5—S bond is involved *(R. Lett, Tet. Lett., 24, 201 (1983))*.

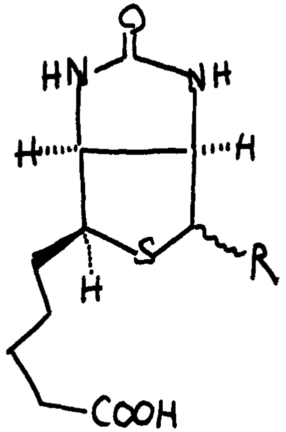


II

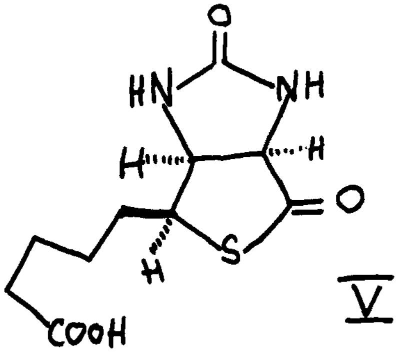
The **application of the Pummerer reaction to Biotin**, surprisingly, appears to have been ignored until a recent report of the first successful conversion of Biotin (I) into the derivatives II, III and IV. The thiolactol II and the thiolactone V are key intermediates in the synthesis of new functionalized derivatives of I.



I



II R = OH
III R = Cl
IV R = OAc

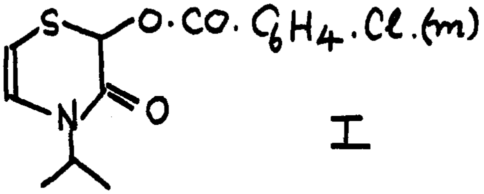


V

The solvolysis of the *m*-chlorobenzoate derivative (I) is shown to occur "with exclusive alkyl oxygen bond fission." The first order rate constants for the reaction were measured at 25°C in a variety of solvents. The *m* value derived from the equation:

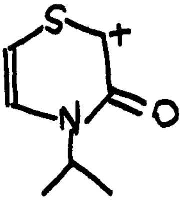
$$\log k - \log k_0 = mY$$

shows a value of 1.53. (Significantly, it is greater than the value for *tert.*-butyl chloride whose $m = 1$ by definition.)



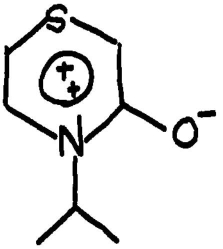
I

The *exclusive* alkyl oxygen fission observed in I along with the high sensitivity of the reaction to solvent polarity is attributed by the authors to the formation of "a very stable carbocation intermediate" (II).



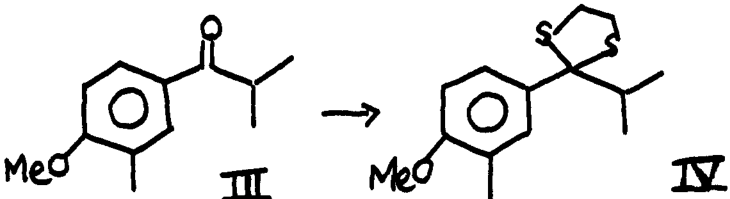
II

They suspect that the cation II may actually exist as the aromatic species III *(R. Lett and Y. Kuroki, Tet. Lett., 23, 5541 (1982)).*

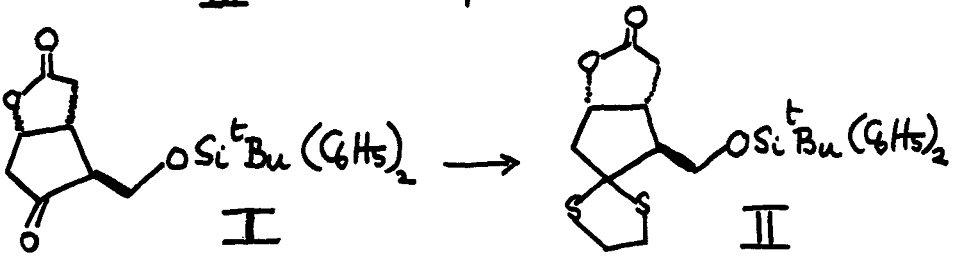


III

Thioketalization using ethane-1,2-dithiol is a common reaction. Even so, the use of protic acids or Lewis acids as condensing agents, sometimes causes eliminations in molecules that carry groups sensitive to acid-catalyzed beta eliminations. In a very elegant and mild procedure, magnesium and zinc triflates are both found to be soluble in methylene chloride and they both effect thioketalization of I to II in greater than 85% yield. The conversion of III to IV was achieved in 100% yield, in refluxing chloroform, in only five hours, using zinc triflate.



III IV



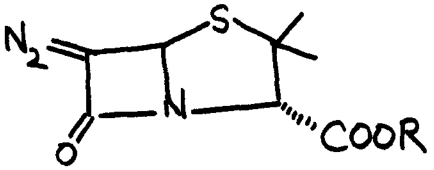
I II

The paper gives full experimental details for preparing magnesium triflate and zinc triflate *(E. J. Corey and K. Shimoji, Tet. Lett., **24**, 169 (1983))*.

An unusual ring expansion resulting from the condensation of the **dithienium perchlorate** (I)

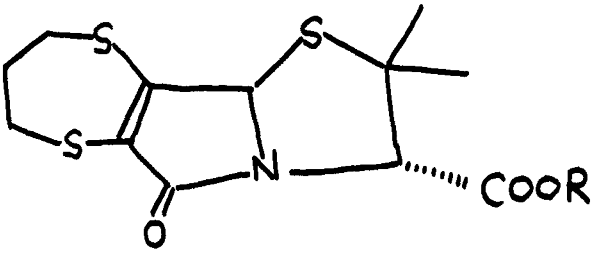
I

with a 6-diazopenicillanate (II) is reported.



II

The reaction was carried out at temperatures ranging between −50° and +180°C in anhydrous acetonitrile solution, giving a complex mixture of products. One compound from this mixture was obtained in a crystalline form in *ca*. 20% yield. Its structure (III) was determined by X-ray crystallography, indicating the unusual ring expansion of the β-lactam ring *(B. W. Bycroft, T. J. King and R. E. Shute, Tet. Lett., **24**, 601 (1983))*.

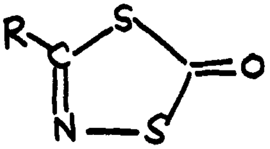


III

In situ generation of the dipolarophile (I)—a **nitrile sulfide**—is achieved by heating the 1,3,4-dithiazol-2-one (II) in mesitylene at 160°C.

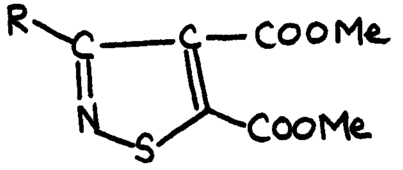
$$R-C\equiv\overset{+}{N}-\overset{-}{S}$$

I



II

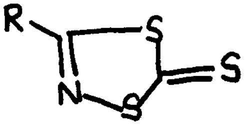
If the thermal expulsion of the carbon oxysulfide is effected in the presence of DMAD (dimethylacetylene dicarboxylate), the product is the isothiazole derivative III.

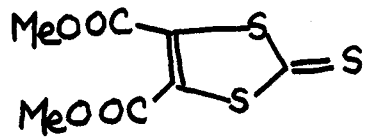


III

However, in striking contrast, no such nitrile sulfide-based products are obtained from IV. Instead, reaction of IV with DMAD gives only V *(D. J. Greig, R. M. Paton, J. G. Rankin, J. F. Ross and J. Crosby, Tet. Lett., 23, 5453 (1982))*.

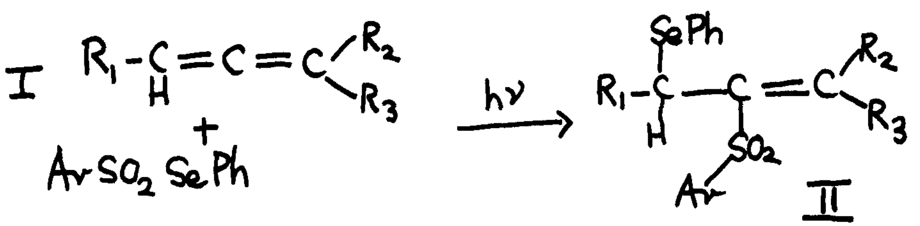
IV



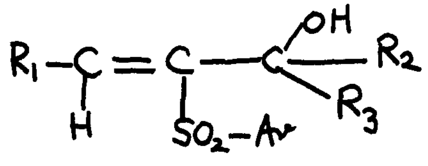


V

A highly **regiospecific addition of Se-Phenylarene selenosulfonates** utilizes the following free-radical addition to an allene:



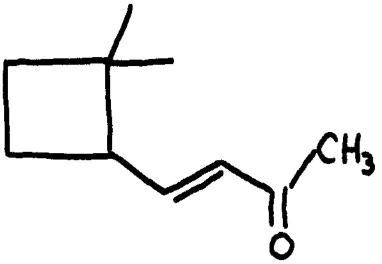
Oxidation of II with hydrogen peroxide affords the allylic alcohol (III) by a (2, 3) sigmatropic rearrangement.



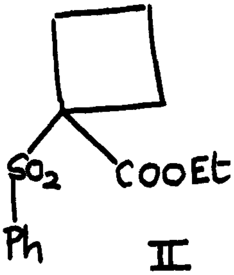
III

The reaction may have synthetic applicability *(Y.-H. Kang and J. L. Kice, Tet. Lett., 23, 5373 (1982))*.

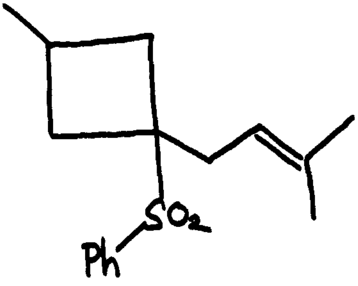
Synthetic exploitation of the **bicyclobutanes carrying the arylsulfonyl function** is further illustrated by another natural product Junionone (I). Following the approach illustrated in the earlier communication, the author reports the synthesis of several other useful intermediates II, III, IV and V which can also be turned to advantage in other natural-product syntheses *(Y. Gaoni, Tet. Lett., 23, 5219 (1982))*.



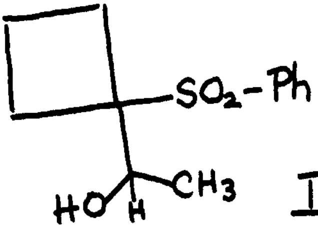
I



II



III



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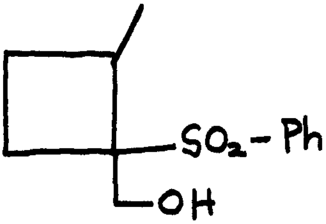
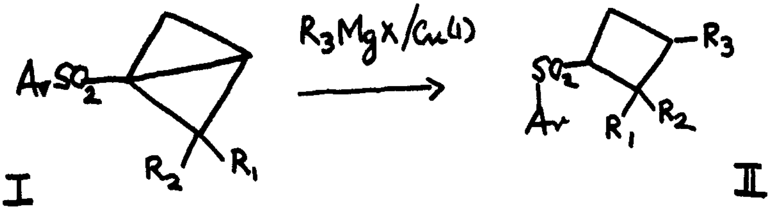
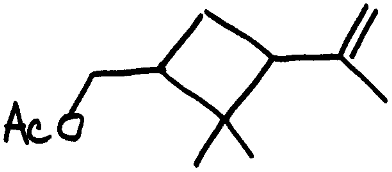


V

Bicyclobutanes incorporating an arylsulfonyl group appear to offer chemoselective reactivity analogous to α,β-unsaturated sulfones, e.g., interesting conjugate additions of a variety of organocopper reagents to I give II.

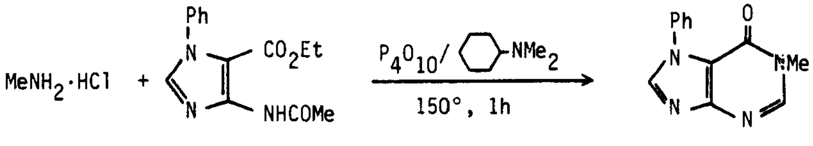


Exploiting this feature of I, and the α-sulfonyl carbanion derivable from II, offers a clever synthesis of III which is the racemic form of the sex pheromone of the citrus mealy bug *Planococcus citri (Y. Gaoni, Tet. Lett., 23, 5215 (1982)).*



III

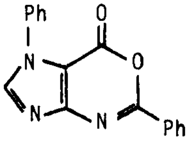
P_4O_{10} in organic synthesis. Twenty-three 1,2,-dihydro-6H-purin-6-ones were prepared in the cyclocondensation of ethyl acylaminoimidazolecarboxylates (e.g. **1**) with amine hydrochlorides and P_4O_{10} as in the example below:



1

55%

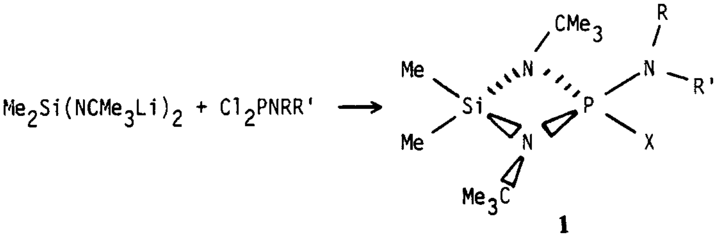
Three imidazooxazinones **2** were prepared in a similar manner from **1** where Me is replaced by a bulky group such as Ph:



2

*(F. E. Nielsen and E. B. Pederson, Tetrahedron, **38**, 1435 (1982)).*

Aminophosphine rotamers. Compounds of type **1** prepared as shown show nmr evidence of hindered rotation about the P—N bond at ambient temperature.

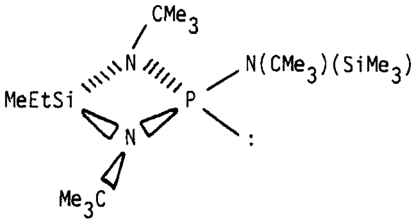


1

R=R'=Me, Me_2CH, Me_3C, Me_3Si, X = lone pair

When R = Me_3Si and R' = Me_3C, a pair of E/Z rotamers could be separated and their structures were characterized by nmr spectroscopy and x-ray diffraction means.

The measured P—N rotation barriers are the highest that have been reported. The four possible isomers of **2** were also prepared.



2

Reaction of **1** with S, Se and MeI gave **1** (X = S, Se, Me^+, respectively) which all showed hindered rotation about the P—N bond below 0° *(O. J. Scherer, M. Puettmann, C. Krueger and G. Wolmershaeuser, Chem. Ber., 115, 2076 (1982)).*

PPh_3 more basic than PMe_3 in gas phase. Using a pulse-electron, high-ion-source pressure mass spectrometer, the kinetics leading to equilibrium (1) were studied

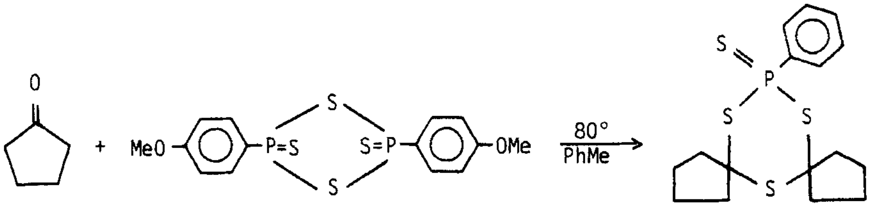
$$BH^+ + B' = B + B'H^+ \qquad (1)$$

and the equilibrium constants for the equilibrium itself were determined for B = PMe_3 and B′ = PMe_2Ph, $PMePh_2$ and PPh_3. The decrease in gas-phase basicity in the order

$$PMe_3 > PPhMe_2 > PPh_2Me > PPh_3$$

parallels the measured decrease in vertical ionization potentials in the gas-phase photoelectron spectra of the P lone pairs for this series. The reversal of this trend from that observed in solution could arise from unfavorable solvation of phenylphosphonium species. The gas-phase basicity trend in the phosphine is opposite to that for the gases Me_2PhN and Me_3N. This result may stem from stabilization of the $HPMe_{3-n}Ph_n^+$ by pi conjugation of the Ph ring with valence orbitals, some of which are empty for phosphorus but not for nitrogen *(S. Ikuta, P. Kebarle, G. Bancroft, G. Michael, T. Chan and R. J. Puddephatt, J. Am. Chem. Soc., 104, 5899 (1982)).*

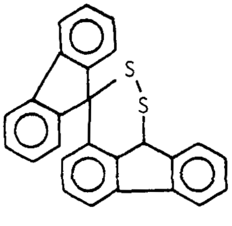
Thionation of ketones with Lawesson's reagent. Ketones such as cyclopentanone undergo cyclocondensation to **1** with Lawesson's reagent (reaction (1)), but similar



(1)

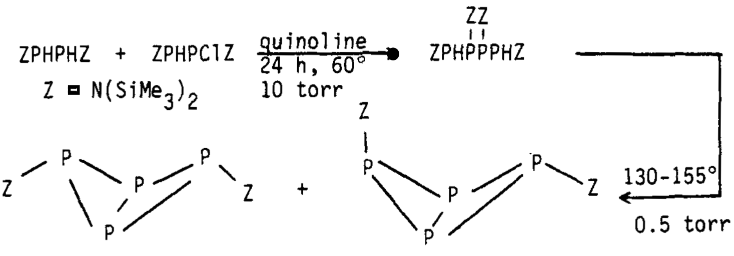
1 (51%)

treatment of 3-methyl-2-cyclohexen-1-one at 60° for 1 h gave the corresponding thione in 86% yield. Fluorenone at 80° for 10 h in the presence of Lawesson's reagent also gave the corresponding thione which on standing overnight in solution gave 55% of the dimer **2** whose structure was determined by x-ray diffraction techniques *(S. Scheibye, R. Shabana, S. O. Lawesson and C. Roemming, Tetrahedron, 38, 993 (1982)).*



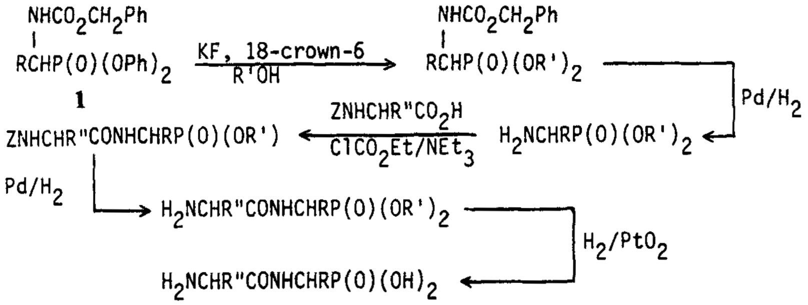
2

The first tetraphosphabicyclobutane. The pathway below leads to the two isomers of the title system **1a** and **1b**. The structure of **1b** was confirmed by x-ray diffraction means *(E. Niecke, R. Ruger and R. Krebs, Angew. Chem., 94, 553 (1982)).*



1a **1b**

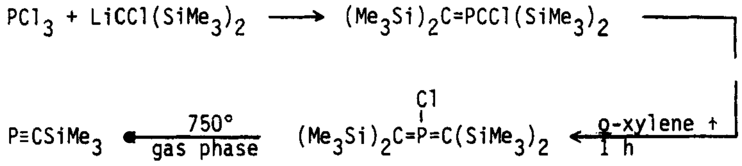
Phosphonopeptide synthesis via diphenylphosphonate transesterification. Employing KF/crown ether, precursor **1** is transesterified in good yield (45–96%) with a variety



of alkyl alcohols in the scheme above. The POR functionality is then reduced in the final step to afford the phosphonopeptide *(J. Szewczyk, B. Lejczak and P. Kafarsky, Synthesis, **409**, 412 (1982)).*

Triple Michaelis-Arbuzov reaction of a $P(OEt)_3$ complex. In the presence of I^- or CN^-, η^5-$C_5R_5M[P(OMe)_3]_3^{+2}$ (M = Co, Rh; R = Me, H) sequentially displaces MeI or MeCN three times to give the corresponding η^5-$C_5R_5M[P(O)(OMe)_2]_3^{-1}$ complex. The anionic complex behaves as a tridentate ligand (L^{-1}) *via* the negatively charged phosphoryl oxygens with metals M^{n+} such as Co^{+2}, Ni^{+2}, Cu^{+2}, Cd^{+2}, Mg^{+2} and Bi^{+3} to form $[LML]^{(n-2)+}$. The ligand field strength of L^- in these octahedral complexes is comparable to that of the weak-field fluoride ion *(W. Klaui, H. Otto, W. Eberspach and E. Buchholz, Chem. Ber., **115**, 1922 (1982)).*

The first P-chlorobis(methylene)phosphorane. The title product **1** is formed in the following reaction sequence:

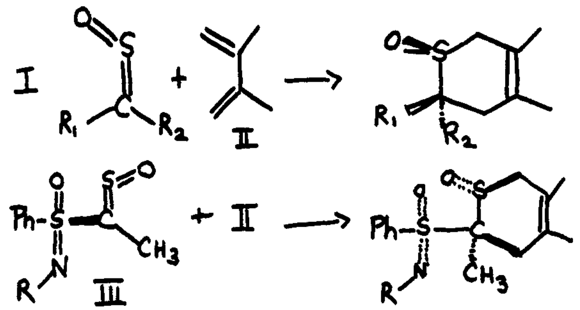


1

(R. Appel and A. Westerhaus, Tet. Lett., 2017 (1982)).

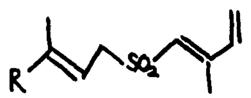
Diasteriomeric phosphorus ligands detected by nmr. The complex $[Ph(BuO)(O)PHgP(O)(OBu)Ph]^0$ displays two slightly different ^{199}Hg chemical shifts about 1100 ppm downfield of external aqueous $HgClO_4$ and two somewhat different $^{1}J^{31}P^{199}Hg$ coupling constants of approximately 5200 Hz. These results are interpreted to signify the presence of two diastereomers. No enantiomeric discrimination was found to occur in the synthesis. The diastereomers could not be separated owing to ligand scrambling reactions *(J. Eichbichler and P. Peringer, J. Organomet. Chem., **231**, 95 (1982)).*

Cycloadditions between 2,3-dimethyl-1,3-butadiene and chiral sulfines is shown to proceed with retention of stereochemistry. The two examples, I and III, shown below are illustrative of this feature:

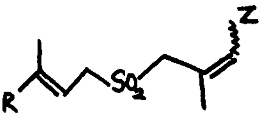


Such asymmetric induction is attributed to the "steric shielding of one diastereotopic face of the sulfine moiety by the N-R substituent" *(P. A. T. W. Porskamp, R. C. Haltiwanger and B. Zwanenberg, Tet. Lett., 24, 2035–38, 1983).*

Michael additions to conjugated dienyl sulfones such as (I) are shown to yield 1,4-addition products (II).



I



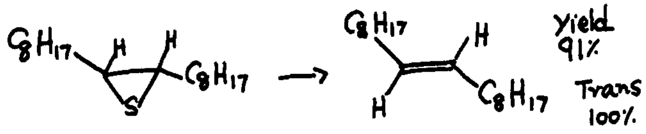
II

The diallyl sulfones thus formed undergo the **Ramberg-Backlund reaction** affording high yields of the trienes (III).

III

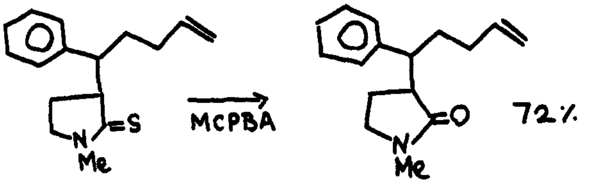
This method of preparing conjugated polyenes via allyl dienyl sulfones appears to hold great synthetic potential *(M. Julia, D. Lave, M. Mulhauser, M. Ramirez-Munoz and D. Uguen, Tet. Lett., 24, 1783–86, 1983).*

Desulfuration of thiiranes to alkenes can now be accomplished in high yields and with considerable degree of stereoselectivity. The following reagents are shown to work well: Raney nickel in ethanol at −40°; lithium and ethylamine at −15°; zinc and acetic acid at 130°; tri-*n*-butyltin hydride at 110°; P_2I_4 in DMF at 80°. The following example is illustrative of the successful conversions:



No alkane was formed in the above example. In others, less than 15% of alkane was obtained. Among the reagents used, Raney nickel in ethanol and lithium and ethylamine gave the most alkanes *(J. R. Schander, J. N. Denis and A. Krief, Tet. Lett., **24**, 1657-60 1983).*

A rapid, mild and selective reaction for the **conversion of thioamides into amides,** uses MCPBA (*m*-chloroperoxybenzoic acid) as oxidant. The reaction proceeds at 0°C or ambient temperature, with total exclusion of any epoxidation and in high yields. The following conversion is illustrative:



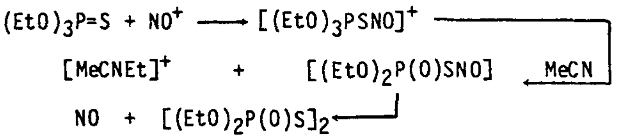
*(K. S. Kochhar, D. A. Cottrell and H. W. Pinnick, Tet. Lett., **24**, 1323-26, 1983).*

P—C bonds from phosphide ions: an improved method. Using $NaAlH_2(OCH_2CH_2OMe)_2$ (SDMA), phosphide ion is rapidly generated from $Ph_2P(O)H$ which then nucleophilically attacks a variety of RX to give the corresponding phosphine oxide in moderate-to-good isolated yields, which increase in the order

$$Ph_2P(O)H \xrightarrow{SDMA} Ph_2P(O)^- \xrightarrow{RX} Ph_2P(O)R$$

Cl < Br < I when R is alkyl. Furthermore, primary RX react faster than secondary RX which require more vigorous conditions. SDMA is a superior reagent for this reaction compared to $NaNH_2$ or $LiAlH_4$ as judged from the product yields. Addition of NaI further improves the yields. ROTs also functions well in this reaction. Other phosphorus reagents which can be used are MePhP(O)H and $PhPH_2$, the latter giving PhP(H)R in excellent yields *(M. Yamshita, N. Suzuki, M. Yamada, Y. Soeda, H. Yamashita, K. Nakatani, T. Oshikawa and S. Inokawa, Bull. Chem. Soc. Jpn., **56**, 219 (1983)).*

Oxidation Pathways for $(EtO)_3P{=}S$ and $Ph_3P{=}S$. The commercial use of compounds of the types in the title as inhibitors of corrosion of iron and oxidation of lubricating oils renders their behavior under oxidizing conditions of interest. Evidence is presented for the dominance of the reaction sequence below for the



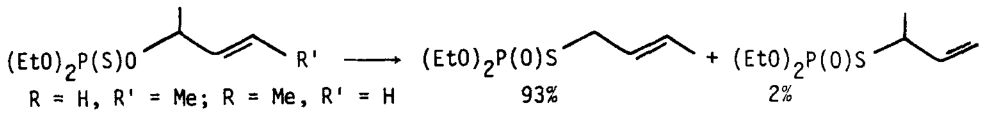
$$(EtO)_3P{=}S + NO^+ \longrightarrow [(EtO)_3PSNO]^+ \xrightarrow{MeCN} [MeCNEt]^+ + [(EtO)_2P(O)SNO] \longrightarrow NO + [(EtO)_2P(O)S]_2$$

oxidation of $(EtO)_3P{=}S$ with $NO^+BF_4^-$ in MeCN as solvent. With $Ph_3P{=}S$ under the same conditions, the reaction below occurs, forming the dicationic dimer which

$$2Ph_3P{=}S + 2NO^+BF_4^- \rightarrow [Ph_3PSSPPh_3][BF_4]_2 + 2NO$$

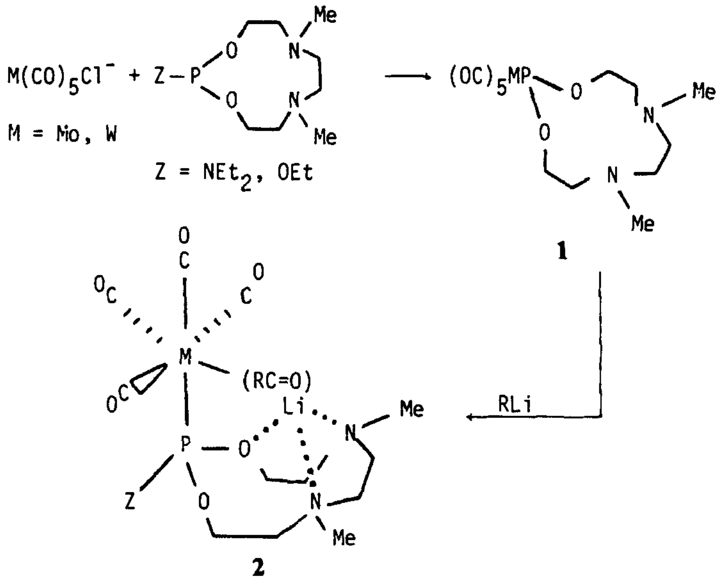
is relatively stable in solution but decomposes upon attempted isolation. The dication can also be produced electrochemically *via* a dimeric cation radical *(R. L. Blankespoor, M. P. Doyle, D. J. Smith, D. A. Van Dyke and M. J. Waldyke, J. Org. Chem., 48, 1176 (1983)).*

Palladium-catalyzed thiono–thiolo allylic rearrangement: a different result. Although thermal rearrangement has been observed to yield the allylic inversion product and catalysis by protic acids has been found to give the allylic retention product selectively, Pd(O) is here reported to provide mainly the products in which the S atom is bound to the least substituted carbon regardless of the substitution pattern of the allylic substituent. Support is given for the suggestion of the presence of a π-allylpalladium intermediate which breaks down to form the thermodynamically stable regio- and stereoisomers of the organophosphorus product.

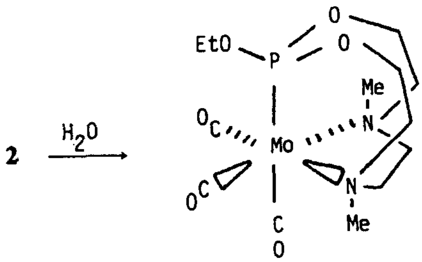


In addition to the high regioselectivity, the Pd(O) catalyzed rearrangement proceeds in high yield with a variety of substituents on phosphorus or the allylic substituent *(Y. Tamaru, Z. Yoshida, Y. Yamada, K. Mukai and H. Yoshioka, J. Org. Chem., 48, 1293 (1983)).*

Novel potential activation of coordinated CO for nucleophilic attack. The crown ether functions as a complexing site for the Li^+ cation in the reaction sequence shown. Intermediate **1** is a colorless oil which in THF with lithium benzoylate or acylate forms crystalline complexes in essentially quantitative yield. For M = Mo



and R = Ph, **2** was structured by x-ray diffraction and found to be dimeric. In the dimer the two complexes are joined *via* two PhCO—Li$^+$ interactions. Molecular weight studies reveal **2** to be monomeric in benzene. In the presence of H_2O the following reaction occurs

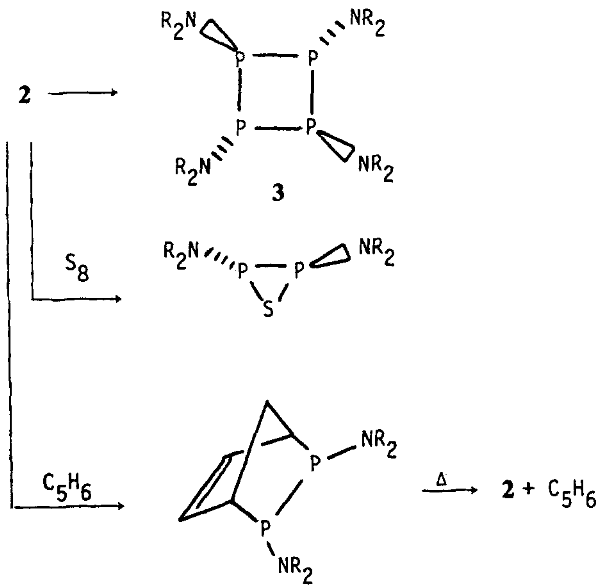


*(J. Powell, K. S. Ng, W. W. Nq and S. C. Nyburg, J. Organomet. Chem., **243**, C1 (1983)).*

A Pyrophoric red diphosphene. Treatment of **1** with base gives the ruby red liquid **2**. Although **2** is stable for days in solution, it dimerizes within hours to crystalline **3**

$$\underset{\mathbf{1}}{R_2N(H)P\text{-}P(Cl)NR_2} \xrightarrow[R\ =\ SiMe_3]{LiN(\underline{t}\text{-}Bu)R} \underset{\mathbf{2}\ (\delta^{31}P\ =\ 572)}{R_2NP{=}PNR_2}$$

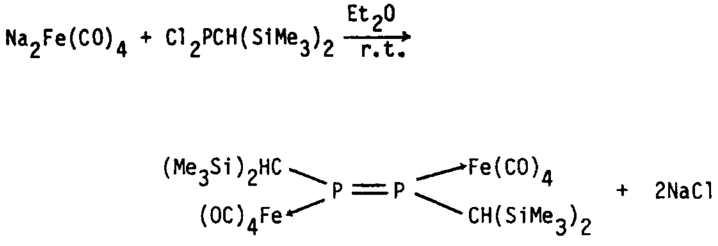
in the absence of solvent. Sulfur or cyclopentadiene yield the cycloaddition products shown. Heating the C_5H_6 reaction product of **2** readily yields the reactants,



demonstrating the utility of the adduct as a stable source of **2** *(E. Niecke and R. Ruger, Angew. Chem. Int. Ed., 22, 155 (1983)).*

$[Ph_2P(S)]_3C^{1-}$: a mesomerically stabilized anion. The title anion is a novel ligand which in the presence of metal halides functions as a six-electron donor *via* the sulfur atoms ($C[PPh_2S]_3M$). The partial delocalization of electronic charge of the central carbon on to the substituents is supported by the planar structure of the anion determined here by x-ray crystallography for the tetra-*n*-butylammonium salt. Interestingly in the solid state, this anion possesses a conformation (similar to its parent $[Ph_2P(S)_3]CH$) in which two sulfurs are "up" and one is "down" for steric reasons *(S. O. Grim, R. D. Gilardi and S. A. Sangokoca, Angew. Chem. Int. Ed., 22, 254 (1983)).*

A diphosphene bridged metal complex. The one-step reaction shown leads to the stable red-brown complex in 50% yield. The structure of this novel complex determined by X-ray means reveals a rectangular planar array of phosphorus, iron and carbon atoms with the nearly trigonal bipyramidal iron atoms *trans*.



$$Na_2Fe(CO)_4 + Cl_2PCH(SiMe_3)_2 \xrightarrow[r.t.]{Et_2O}$$

This is the first reported example of a complex in which the group 5b multiple bond is unbridged by a transition metal atom. The P—P distance of 2.039(1) Å suggests that there is very little phosphorus lone pair involvement in the P=P bond *(K. M. Flynn, M. M. Olmstead and P. P. Power, J. Am. Chem. Soc., **105**, 2085 (1983))*.