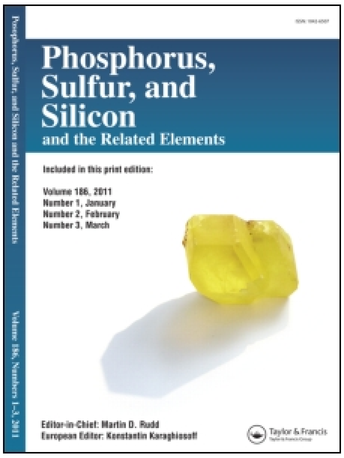

Phosphorus, Sulfur, and Silicon and the Related Elements
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Literature Highlights

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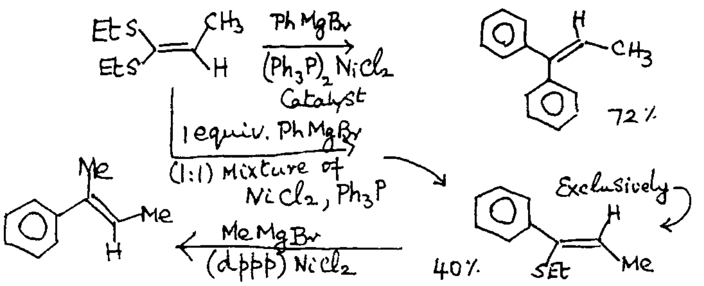
LITERATURE HIGHLIGHTS

Contributions may be forwarded in duplicate to any one of the editors. Drawings and structures must be neatly and compactly prepared in ink for *direct* photoreproduction. All abstracts must be in English with double-spaced, typed text, including complete reference source of the abstract at the end. Preparers are not acknowledged.

A new method for **regio- and stereoselective olefin synthesis** is reported. The procedure can be illustrated by the following reactions:



In an indirect fashion, it can also be construed as a method for reducing carboxylic acids (the bisalkylthioalkenes are masked acid functions) into masked carbonyl groups (monoalkylthioalkenes). *(E. Wenkert and T. W. Ferreira, Chem. Commun., 840, 1982).*

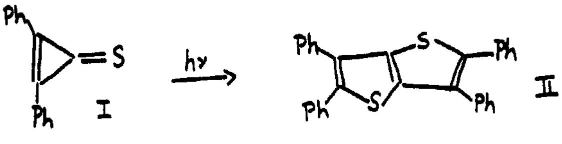
A similar outcome is seen in the overall transformations of primary alkyl phenyl sulfides into **esters and carboxylic acids** *(C. C. Fortes, H. C. Fortes, and D. C. R. G.*

Goncal, Chem. Commun., 1982, 857):

$$RCH_2SPh \xrightarrow[py]{SOCl_2} RCCl_2SPh \xrightarrow[H_2O]{MeOH} RCO_2Me$$

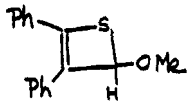
$$RCH_2CH_2SPh \xrightarrow[py]{SOCl_2} RCH{=}CClPh \xrightarrow[HCO_2H]{Hg(OAc)_2} RCH_2CO_2H$$

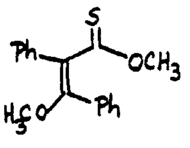
Photochemical excitation of diphenylcyclopropenethione (I) forms diphenylacetylene (by α-cleavage) *only* when oxygen is present in the medium. Irradiation of I in deaerated benzene gave only II.



However, irradiation in methanol gave in addition to II, the thiete III and the thioester IV.

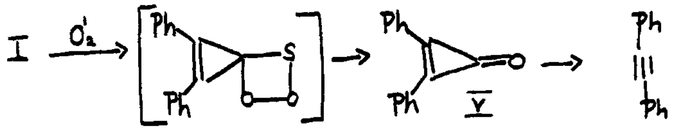
III





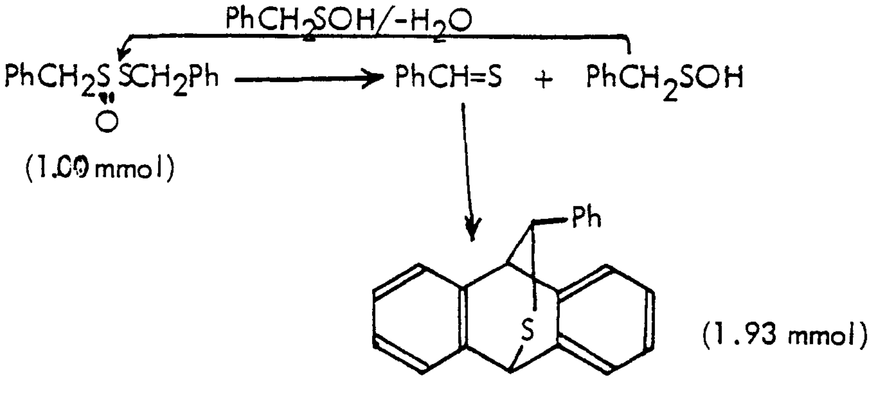
IV

Formation of III and IV is unusual and interesting pathways for their formation are offered by the authors. When I was irradiated in benzene, ethanol or acetonitrile solution using *unpurified* nitrogen, diphenylacetylene was obtained in 80% yield. None of the other products was found. The authors convincingly demonstrate the intermediacy of V in the formation of the acetylene.



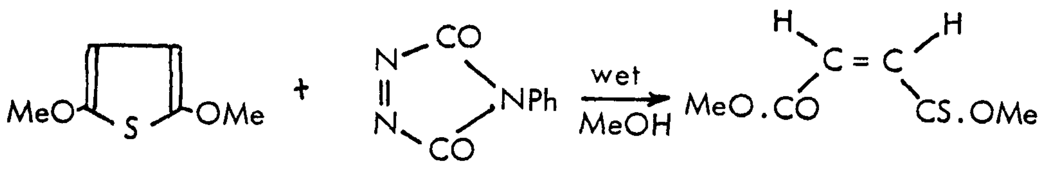
This paper makes a significant contribution to the photochemistry of thioketones *(S. Singh, M. M. Bhadbhade, K. Venkatesan and V. Ramamurthy, J. Org. Chem., 47 3550–53, 1982).*

Thioacetaldehyde and thiobenzaldehyde have been generated by thermolysis of an alkyl methanethiolsulfinate or benzenethiolsulfinate in toluene at 100° during 1 h:

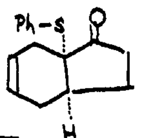


Although building on earlier knowledge, a preparatively useful outcome of this work is the use of the anthracene adduct itself as a source of thioaldehydes. Thus, when it is heated in a sealed tube with an alkene, ene reaction adducts are formed. Diels–Alder adducts are formed with dienes. The advantage of this procedure is that the thioaldehyde can be generated free from other reactive species *(J. E. Baldwin and R. C. G. Lopez, Chem. Commun., 1982, 1029).*

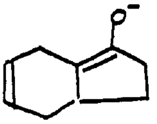
Other simple thiocarbonyl compounds are also more readily accessible through recent studies. **Dimethyl monothionomaleate** is formed by the reaction of 2,5-dimethoxythiophene with N-phenyltriazolin-2,5-dione (PTAD) as an orange oil, and can be rearranged to the corresponding fumarate (an orange solid, mp 30–32°) by warming *(D. Del Mazza, Chem. Commun., 1982, 1033)*:



A clever application of the strategic location of a phenylthio group in tetrahydroindanones. In the direct **alkylation of 5,6-tetrahydroindanones**, the incorporation of a phenylthio group at the bridgehead offers regio and stereochemical control. When compound I reacts with lithium in liquid ammonia, the anion II is formed. Alkylation of II with methyl bromoacetate (III) leads predominantly to the cis indanone (IV) in 60% yield.

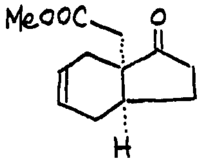


I

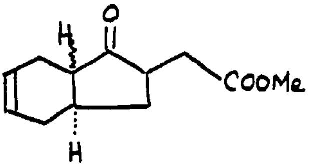


II

Such stereoselectivity is in striking contrast to the mixture of cis and trans stereoisomers obtained (cis/trans: 3/2 of V) when the alkylation was effected using lithium diisopropylamide and III. The synthetic utility of indanones is greatly enhanced by the angular phenylthio group as a valuable handle for stereochemical control in alkylations *(T. V. Lee and J. Toczek, Chem. Commun., 968, 1982).*

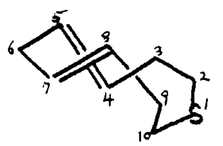


IV



V

The intriguing possibility of producing **chiral (E,E)Thiacyclodeca-4,7-diene** (I) is reported. However, no optical activity was found in the compound—suggesting that conformational "enantiomerization" has only a low energy barrier.



I

The synthesis of I begins from enantiomerically pure D-mannitol, thereby ensuring enantiomeric integrity in the final product by appropriate reaction conditions. A 3-methyl derivative (II) of I is also reported. The ^{13}C nmr spectrum of II measured at −30°C reveals "two unequally populated diastereomeric conformers whose interconversion is frozen (in the nmr time scale) at this temperature." Accurate line-shape analysis in the −32 to 60°C range established the barrier for enantiomerization to be on the order of 11 kcal/mol.

This publication appears to be the first study into the stereochemical integrity of such medium-size ring dienes *(V. Cere, E. Dalcanale, C. Paolucci, S. Pollicino, E. Sandri, L. Lunazzi and A. Fava, J. Org. Chem., 47, 3540–44, 1982).*

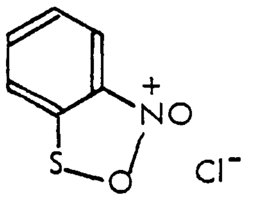
Sulfinyl halides are generally liquids of limited stability, and an explosion has been reported during attempted distillation of toluene-*p*-sulfinyl chloride, but a convenient route to **sulfinate esters** which avoids the use of a sulfinyl halide has been advocated. Dehydration of a sulfinic acid using dicyclohexylcarbodiimide yields the corresponding sulfinylsulfone, which reacts with an alcohol to give the required alkyl arenesulfinate in good yield. The procedure should be generally applicable *(R. B. Boar and A. C. Patel, Synthesis, 1982, 584)*:

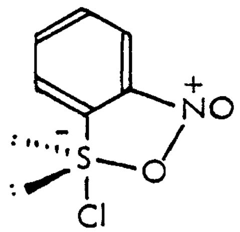
$$\mathrm{TsSO_2H} \xrightarrow{\mathrm{DCCI}} \mathrm{TsSO_2SOTs} \xrightarrow{\mathrm{ROH}} \mathrm{TsSOOR}$$

Much of the organosulfur chemical literature of the past ten years has featured the results of mechanistic studies with representative sulfur functional groups. One well-studied reaction, but still generating interesting results, is the $\mathrm{Ad_E2}$ addition of arenesulfenyl halides to alkenes. Although **^{36}Cl—$^{35/37}$Cl exchange** is insignificant over 24 h for the system

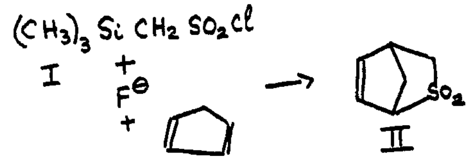
$$\mathrm{ArS^{36}Cl} + \mathrm{LiCl} \rightleftharpoons \mathrm{ArSCl} + \mathrm{Li^{36}Cl}$$

in acetic acid for most common aryl groups, the presence of an *o*-nitro group in the aryl moiety leads to exchange which is so fast that accurate rate data cannot be obtained. It remains to be established whether anchimeric assistance involves the ion-pair or sulfurane intermediates *(L. A. Andreeva, N. S. Zefirov, V. M. Fedoseev, and V. S. Churilin, Tet. Let., 1982, 23, 3797)*:

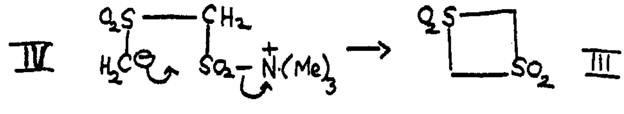




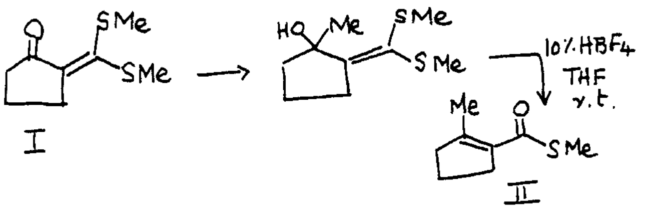
Sulfene ($\mathrm{CH_2{=}SO_2}$) is a useful addend for numerous (2 + 2) and (2 + 4) cycloaddition reactions. It has been generated readily from the reaction of triethylamine and methanesulfonyl chloride. An impressive new procedure generates sulfene *at ambient temperatures* and consistently gives superior yields in cycloaddition reactions, according to authors Block and Aslam. Trimethylsilyl methanesulfonyl chloride (I) was prepared from chloromethyltrimethylsilane and thiourea, via oxidation with chlorine in water at 0°. When treated with an equivalent amount of cesium fluoride in dry acetonitrile solutions, I afforded sulfene which was trapped readily by *in situ* cycloaddition with dienes. (vide infra.)



This mode of generation of sulfene gave no dimer (III) whereas the reaction between mesyl chloride and triethylamine did. The authors rationalize this by the cyclization of a dimeric amine complex (IV) in the latter reaction *(E. Block and M. Aslam, Tet. Let., 23, 4203-06, 1982).*

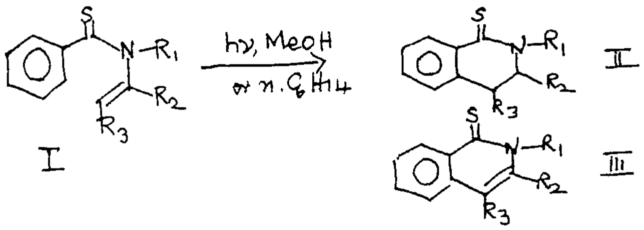


Carbonyl transpositions are of considerable synthetic value. The conversion of an alpha oxoketene dithioacetal (I) into a beta-substituted alpha,beta-unsaturated thioester (II) is reported in this study.

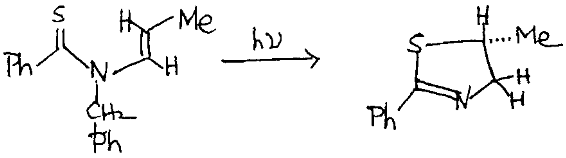


Numerous other examples of this transformation are reported. The yields of the thioester range between 50 & 80%. The method appears to have good synthetic potential *(R. K. Dieter and Y. Jenkitkasemwong, Tet. Let., 23, 3747-50, 1982).*

Photochemical cyclizations of thioenamides form isoquinolinethione derivatives. Two interesting aspects to such cyclizations are presented. N-alkylthioenamides such as (I) lead to tetrahydroisoquinolinethiones (II) and isoquinolinethiones (III).

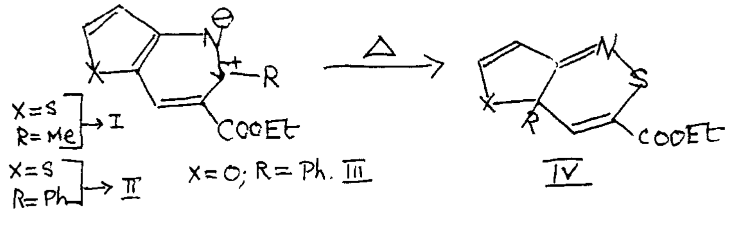


This transformation is described as a "photochemical electrocyclic ring closure of a 6-electron system." However, an *N*-benzyl thioenamide (IV) leads to a thiazoline derivative (V):

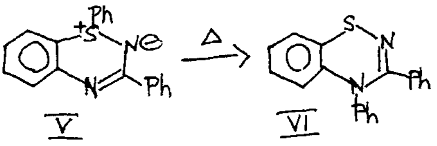


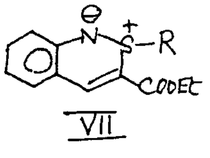
This process is described as "radical recombination and ultimate hydrogen abstraction" *(A. Couture, R. Dubiez and A. L. Combier, Chem. Commun., 842, 1982).*

Some unusual **thermal rearrangements of sulfonium ylids** are reported. The interesting aspect of these migrations is the disruption of aromaticity in the final product structure. *vide infra*:



The rearrangement, it is suggested, occurs by a (1,4) shift of the sulfur substituent to carbon, or by a (1,4) shift to a ring nitrogen as in the example below:

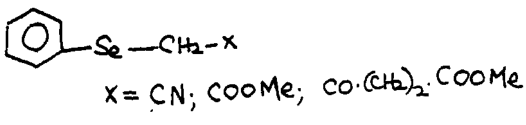




However, 1,4-migration to a benzene ring carbon from sulfur does not occur. Thermolysis of VII leads only to complete degradation of the molecule. This example appears to suggest the absence of the commonly observed 1,2-shift of the Stevens rearrangement in these systems *(R. D. Grant, C. J. Moody, C. W. Rees and S. C. Tsoi, Chem. Commun., 884, 1982).*

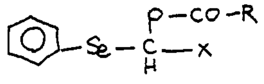
A Pummerer-type rearrangement leading to the formation of a **hemiselenoacetal** is reported for the first time. Compounds of type I (vide infra) were oxidized in

I



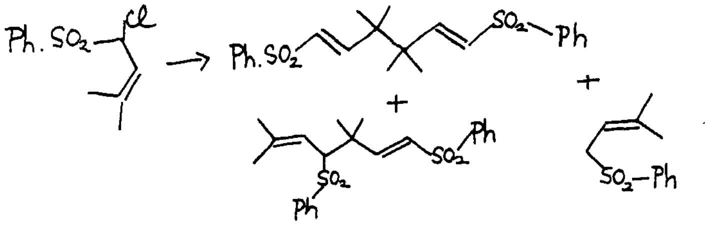
chloroform solution at 0°C using peracids. Diphenyl dieselenide was isolated in 25–35% yields as a by-product. The major product was II.

II



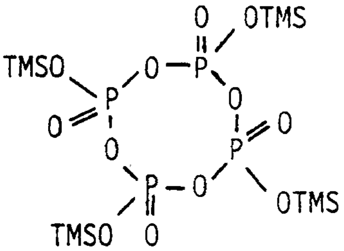
The authors did not isolate any selenoxide in the reaction; the *only* selenium-containing aliphatic product was the selenoacetal II. Yields of the acetal ranged between 37 and 58% *(C. Galambos and V. Simonidesz, Tet. Let., **23**, 4371–72, 1982).*

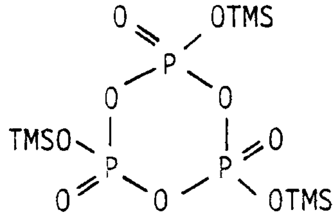
Allylic alpha halosulfones undergo allylic coupling on reduction with tri-n-butyltin hydride. In addition, they undergo allylic coupling as shown below:

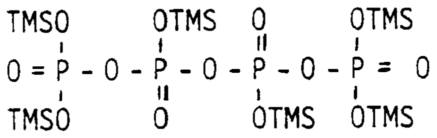


The reduction was carried out in boiling benzene in the presence of azobisisobutyronitrile (AIBN). This study is one of a few in recent years, to focus on the formation of alpha sulfonyl radicals and may lead to a more extensive understanding of the stability of such radicals *(M. Julia, C. Rolando and J. N. Verpeaux, Tet. Let., **23**, 4319–20, 1982).*

Trimethylsilyl esters of tetraphosphoric acid (PPSE): a convenient condensation reagent. In excess $(Me_3Si)_2O$, P_4O_{10} cleaves to form mixtures of cyclic and linear PPSE's, whose composition as analyzed from ^{31}P nmr spectra are solvent dependent. These mixtures function as an improved reagent under milder conditions for the





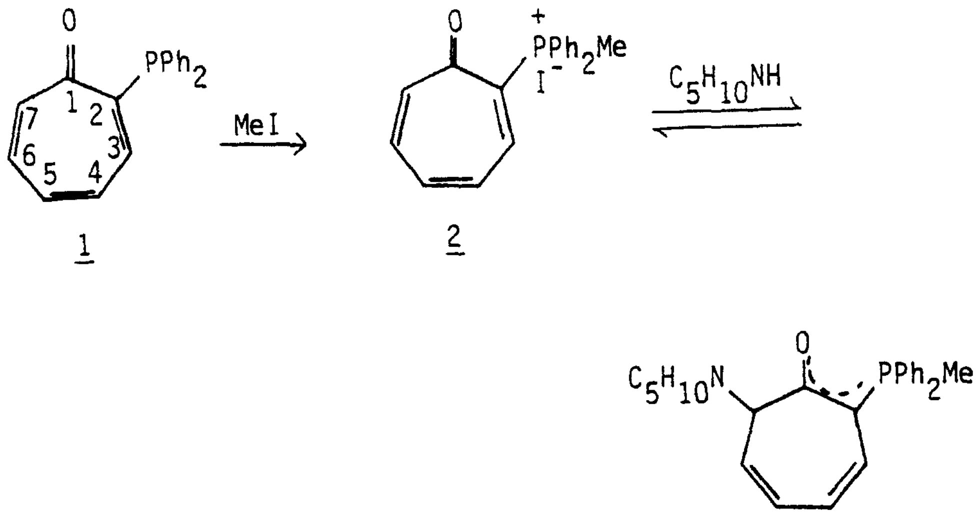


$$O=\underset{TMSO}{\overset{TMSO}{P}}-O-\underset{\|}{\overset{OTMS}{P}}-O-\underset{OTMS}{\overset{\|}{P}}-O-\underset{OTMS}{\overset{OTMS}{P}}=O$$

Phillips benzimadazole (and analogs), Fischer indol, Bischler-Napieralski isoquinoline and Pechmann coumarin syntheses. Preliminary experiments with the P_4O_{10} reaction with dry silica gel indicate that such "heterogenized PPSE" holds substantial promise for similar syntheses *(K. Yamamoto and H. Watanabe, Chem. Letters, 1225, 1982).*

Presence of $H_3P \cdots H—X$ in gas phase. Using the recently developed technique of Fourier-transform microwave spectroscopy, rotational emissions of equimolar mixtures of gaseous PH_3 and HX (X = Cl, Br) pulsed supersonically into a Fabry–Perot cavity were analyzed. The rotational spectra of the mixtures are characteristic of prolate symmetrical top molecules and the spectroscopic constants are consistent with hydrogen-bonded species in which the H—X molecule is colinear with the C_{3v} axis of PH_3. Moreover, the data exclude significant contributions of $PH_4^+ \ X^-$ to the valence bond description of these gas-phase dimers *(A. C. Legon and L. C. Willoughby, Chem. Commun., 997, 1982).*

A peculiar acylphosphorane. Although 2-iodo or 2-chlorotropone with PPh_3 or $P(n\text{-}Bu)_3$ in a variety of solvents under N_2 leads to intractable tars, 1 in the presence of MeI gives 2 as indicated by uv-visible, ^1H and ^{13}C nmr spectroscopy. Addition of piperidine to 2 in dry $(CD_3)_2SO$ under N_2 causes the uv bands of orange-brown 2 to disappear with the formation of a dark green solution whose uv-visible, ^1H and ^{13}C nmr spectra are consistent with the formulation shown for 3. Compound 3 can be isolated as a dark green solid as long as $C_5H_{10}NH$ is present in trace quantities. Confirmatory of the formation of the phosphorane 3 is the 9.6 ppm upfield shift of the ^{31}P resonance from 2 which is taken to be suggestive of less positive charge on phosphorus in 3. The increase in P—C-2 coupling and the high-field shift of ^{13}C-2



1 2 3

from 2 to 3 are consistent with the extended conjugation from O to P as shown in 3 *(M. Cavazza, G. Morganti, G. A. Veracini and F. Pietra, Tet. Letters, 4119, 1982).*

Cobalt(0) complexes of $P(OR)_3$. In the presence of $P(OR)_3$ (R = Me, Et, *i*-Pr), the new paramagnetic d^9 complexes shown in the reactions below are made in good yields from the cobalt(0) substrates. The mononuclear character of these complexes

$$\mathrm{Co(MeCN)_2(EF)_2 + 3P(OR)_3 \rightarrow Co(EF)[P(OR)_3]_3 + 2MeCN + EF}$$

yellow

EF = ethyl fumarate

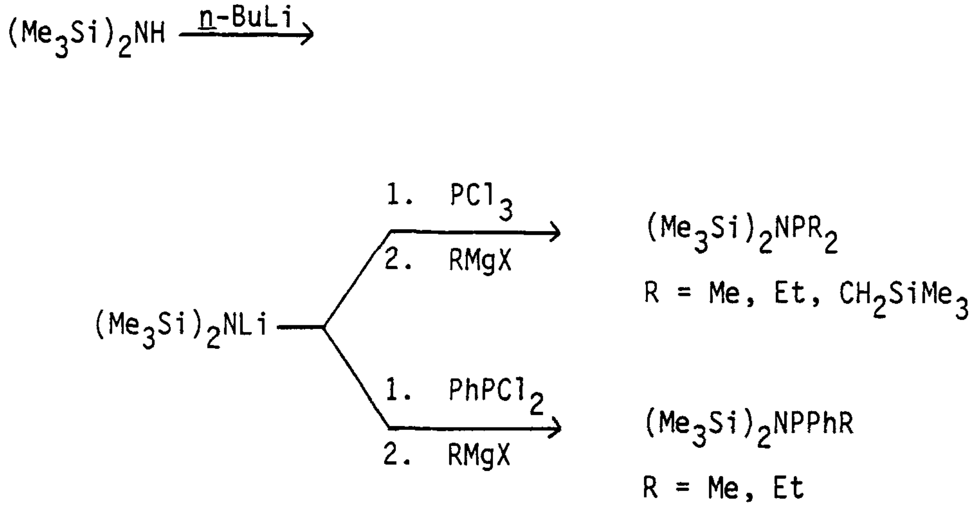
$$\mathrm{Co(MeCN)_2(MA)_2 + 3P(OR)_3 + MA \rightarrow Co(MA)[P(OR)_3]_3 + 2MA + 2MeCN}$$

red

MA = maleic anhydride

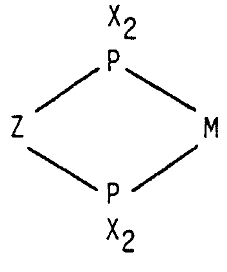
in solution and in the solid state are confirmed by cryoscopic molecular weight measurements and a structure determination of $Co(MA)[P(OMe)_3]_3$ wherein the cobalt appears to be approximately tetrahedrally surrounded by three $P(OMe)_3$ ligands and the olefin linkage of MA. Part of the distortion from tetrahedral geometry is attributed to Jahn-Teller effects. The reactions described herein are of interest in view of the current interest in hydrogenation, carbonylation and polymerization reactions which are catalyzed by cobalt(0) complexes *(G. Agnes, J. C. J. Bart, C. Santini and K. A. Woode, J. Amer. Chem. Soc.,* ***104****, 5254, 1982).*

Convenient synthesis of $(Me_3Si)_2NPRR'$ reagents. The title reagents are of current interest in the synthesis of organo-substituted phosphazene polymers, novel organophosphorus compounds and metal complexes. In this article is described a "one-pot" synthesis of $(Me_3Si)_2NPRR'$ compounds on a relatively large scale (*ca.* 1-2 mol) in 59 to 81% yields:

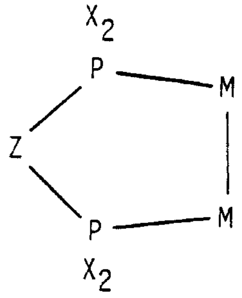


In certain cases it is also possible to obtain monoalkylated products such as $(Me_3Si)_2NP(Cl)CH_2SiMe_3$ *(R. H. Neilson and P. Wisian-Nelson, Inorg. Chem.,* ***21****, 3568, 1982).*

$MeN[P(OMe)_2]_2$: a small-bite bidentate ligand. Ligands of the type $Z(PY_2)_2$ offer the opportunity to prepare and study metal complexes of types A and B. Previous examples of such ligands are $CH_2(PPh_2)_2$, $O[P(OR)_2]_2$ and $MeN(PF_2)_2$ whose



A



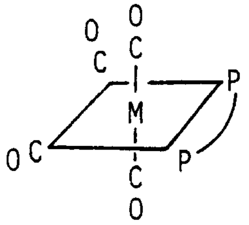
B

ligand properties are described in references cited by the authors. In the present work, the title ligand prepared by the reaction (1), is found to give

$$\mathrm{MeN(PCl_2)_2 + MeOH \xrightarrow{R_3N} Me_2N[P(OMe)_2]_2} \qquad (1)$$

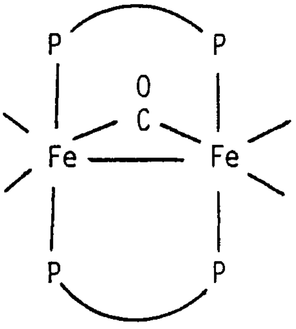
complexes of type A using the synthetic approach in reaction (2). With $Fe(CO)_5$ in

$$\mathrm{(OC)_4M(norbornadiene) + MeN[P(OMe)_2]_2 \rightarrow}$$

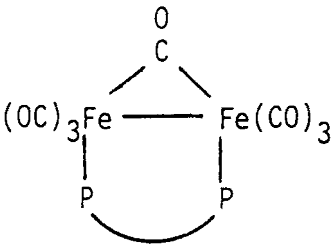


+ norbornadiene (2)

the presence of uv light, 3 is formed but with $Fe_2(CO)_9$ the reaction becomes more



3



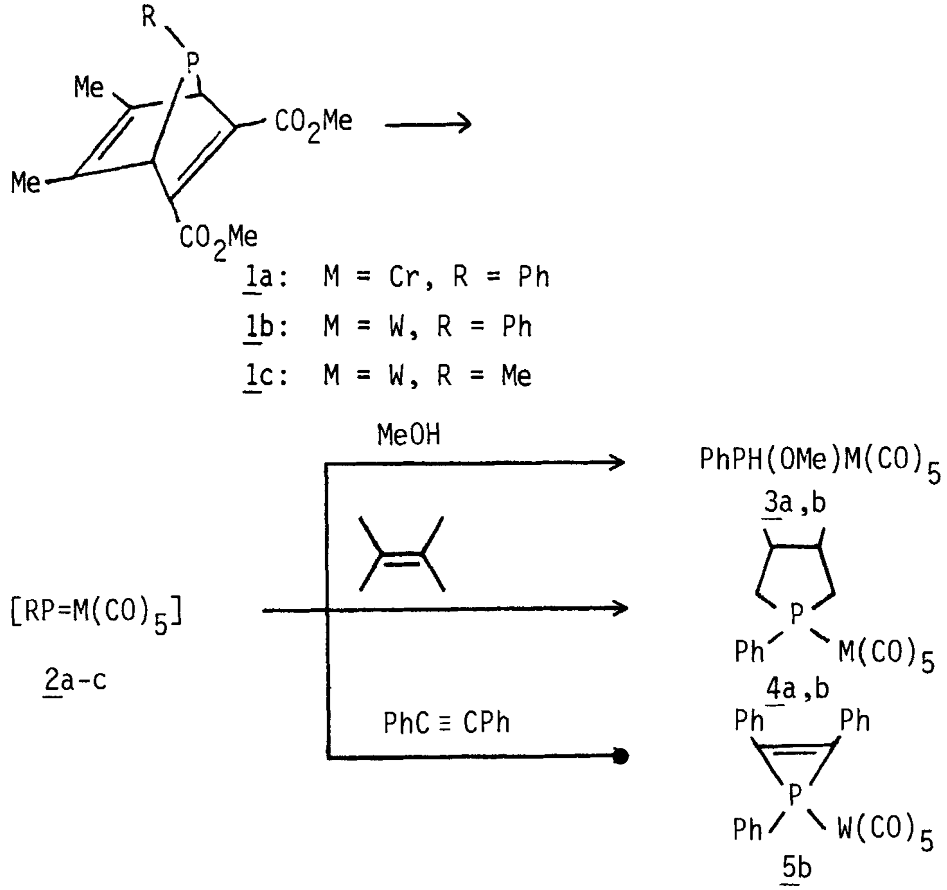
4

complicated. In the presence of excess $Fe_2(CO)_9$ reaction (3) occurs but with

$$Fe_2(CO)_9 + MeN[P(OMe)_2]_2 \rightarrow \underset{4}{MeN[P(OMe)_2]_2Fe_2(CO)_7} \qquad (3)$$

excess ligand several liquid products are formed which could not be separated. Under forcing conditions, however, 3 could be isolated. The structure of 4 determined by x-ray diffraction methods shows a molecular geometry similar to that found by others for $CH_2[PPh_2]_2Fe_2(CO)_7$. The CO stretching frequencies in the complexes described herein are consistently lower than those reported earlier by the authors for analogous complexes of $MeN(PF_2)_2$, which is taken to imply a lower pi acceptor power for the title ligand *(C. M. Brown, J. E. Finholt, R. B. King, J. W. Bibber and J. H. Kim., Inorg. Chem., **21**, 3790, 1982).*

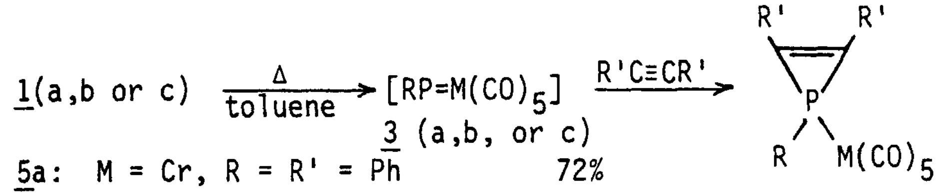
Generation and trapping of PhP=W(CO)$_5$. Although phosphinidenes (RP) are known to function as μ^2-, μ^3- and μ^4-bridging ligands in transition metal complexes, there is no previous report of its coordination as a monodentate ligand. From 1b whose synthesis was reported earlier from the authors' laboratories, it was found that 2b is formed in the mass spectrometer. Thermolysis of 1b in the presence of trapping reagents yielded the complexes 3–5b formed in a novel fashion by trapping of transient 2, but the ligands in these compounds are unknown in the uncoordinated state. Moreover, the synthesis of compounds of type 5b is quite general:



1a: M = Cr, R = Ph

1b: M = W, R = Ph

1c: M = W, R = Me

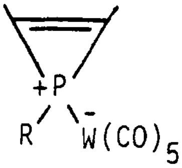


$$1(a,b \text{ or } c) \xrightarrow[\text{toluene}]{\Delta} [RP{=}M(CO)_5] \xrightarrow{R'C{\equiv}CR'}$$

3 (a,b, or c)

5a:	M = Cr, R = R' = Ph	72%
5b:	M = W, R = R' = Ph	64%
5c:	M = W, R = Ph, R' = Et	50%
5d:	M = W, R = Me, R' = Ph	60%
5e:	M = W, R = Me, R' = Et	71%

Although the ^1H nmr, ^{13}C nmr and ir spectral data from 5a–e are surprisingly normal, the ^{31}P chemical resonances are shifted strongly upfield and the latter has also been noted in many three-membered phosphorus rings including phosphiranes. This observation appears to eliminate stabilization of the phosphirene ring by delocalization as in the zwitterion:



Such poor electron delocalization is confirmed by the x-ray structure of 5b which reveals the smallest CPC bond angle known (42.8(2)°), surprisingly long intracyclic P—C bond lengths (1.831(6)Å) and a rather localized intracyclic C=C bond (1.307(6)Å). The stabilization of the phosphirene ring is attributed to the electron withdrawing ability and the bulkiness of the $W(CO)_5$ group *(A. Marinetti and F. Mathey, J. Amer. Chem. Soc., **104**, 4484, 1982).*