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Studies on Low-Coordinated Nitrogen, Phosphorus, Sulfur, and Selenium Compounds

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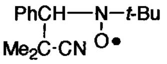
ABSTRACT: *The major studies of my laboratory on heteroatom chemistry are briefly outlined and include the following topics: (1) novel radical reactions to kinetic stabilization of organosulfur and selenium compounds, (2) novel reactions of organophosphorus compounds, (3) reaction of the S atom to stabilization of o-thioquinonemethides, (4) N-nitrosoimines stabilized by heterocycles to hypervalent sulfur compounds, and (5) phosphinidenes (R-P) to kinetic stabilization of low-coordinated organophosphorus compounds.* © 2001 John Wiley & Sons, Inc. Heteroatom Chem 12:183–194, 2001

FROM NOVEL RADICAL REACTIONS TO KINETIC STABILIZATION OF ORGANOSULFUR AND SELENIUM COMPOUNDS

I started working on α,α'-azobisisobutyronitrile (AIBN) in 1953 and found oxygen abstraction reactions (1–5% at 100°C) of nitroarenes [1], azoxybenzene [2], and amine *N*-oxides [2] by 1-cyano-1-methylethyl radicals generated from AIBN. On the assumption that the results are due to the presence of a coordinate bond (N^+-O^-), a reaction of the nitrone $PhCH{=}N(O)Ph$ with AIBN was carried out. However, the extent of the oxygen abstraction was only 0.5%, but an unexpected 1,3-radical adduct to the α-C and O atoms was obtained [3,4]. To my surprise, use of the bulky nitrone **1** ($PhCH{=}N(O)$-t-Bu) afforded an unusually stable nitroxide radical **2** as red crystals in spite of the presence of an α-hydrogen atom, this taking place because of steric inhibition of disproportionation [5]. Therefore, the nitrone **1** has became useful as a spin trapping reagent [6].



$\mathrm{PhCH(CMe_2CN)-N(O^{\bullet})-}t\text{-Bu}$

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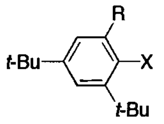
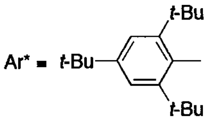


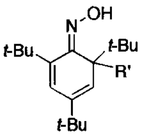
3 (X = NH_2), **10** (X = NS)
4 (X = NO), **18** (R = CN, X = NS)



At the same time, several oxidation reactions of bulky anilines **3** were studied. Oxidation with perbenzoic acid afforded nitrosobenzenes **4** as monomers even in the solid state (green color) because of steric inhibition of the dimerization [7,8]. The nitrosobenzene Ar*NO **4** (R = *t*-Bu) gave an unusual 1,6-radical adduct to the O and *p*-C atoms in reaction with AIBN [9]. Hereafter Ar* denotes the 2,4,6-tri-*tert*-butylphenyl group in this article.

It has been reported that **4** (R = *t*-Bu) afforded a nitroxide radical Ar*RNO· by addition of a primary alkyl radical to the N atom, an arylaminyl radical Ar*(RO)N· by addition of a tertiary alkyl radical to the O atom, and both radicals with a secondary alkyl radical [10], in agreement with the aforementioned results. Thus **4** (R = *t*-Bu) can also be used as a spin trapping reagent.

Reactions of Ar*NO **4** (R = *t*-Bu) with R′MgX gave oximes **5** and **6** via an ionic pathway and an *N*-alkylaniline Ar*NHR′ **7**, depending on the R′ group [11]. The yields of **5** and **6** decrease and increase in the order of R′ = Me, Et, and *i*-Pr, respectively (not produced when R′ = *t*-Bu). The very bulky amine **7** is the main product when R′ = *t*-Bu, a low yield when R′ = *i*-Pr, and no compound **7** is obtained when R′ = Me and Et. The amine **7** was proved to be formed via a single electron transfer mechanism and cannot be prepared by alkylation of **3** (R′ = *t*-Bu), except when R′ = Me or Et.



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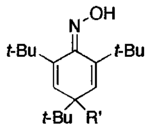

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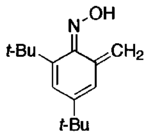

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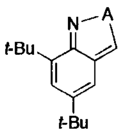
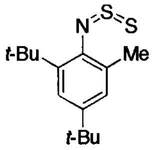


9 (A = O)
16 (A = S)

Heating of **4** (R = Me) afforded a 2,1-benzoxazole **9** [9], formation of which was shown to be due to the existence of an equilibrium with **8**, which was formed by a 1,5-hydrogen shift [12].

Since nitrosobenzenes **4** were monomeric, we tried isolation of a potentially fascinating intermediate, thionitrosobenzene **10**. However, reactions of **3** (R = Me) with SCl_2 in the presence of Et_3N unexpectedly produced the *N*-thiosulfinylaniline **11**, and reaction with **3** (R = *t*-Bu) gave the corresponding cyclized product **12** as very stable crystalline solids, along with sulfur diimide Ar–N = S = N–Ar **13** and Ar–N = S = O **14** (only when R = *t*-Bu) [13]. The 5*H*-1,2,3-benzodithiazole **12** existed in equilibrium with the corresponding open form (analogous to **11**) in solution. Independently, Barton et al. reported formation of a stable *N*-thiosulfinylaniline **15** instead of the expected thionitrosobenzene by reaction of *p*-(dimethylamino)nitrosobenzene with P_2S_5 [14], but **15** was not particularly stable according to our experiment.



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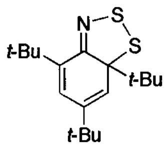

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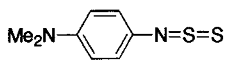

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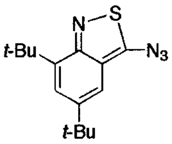
Compounds **11** and **12** were efficiently synthesized using S_2Cl_2 instead of SCl_2 [13]. Thermolysis of **11** gave 2,1-benzothiazole **16**, analogous to **9**, suggesting formation of **10** (R = Me) as an intermediate, and photolyses of **11** and **12** afforded the corresponding sulfur diimide **13** [15]. Photolysis of **11** produced a compound that exhibited a band at 473 nm in an EPA matrix at 77 K [15]. The absorption band was attributed to that of **10** (R = Me) as shown subsequently. Desulfurization of **12** with Ph_3P produced the corresponding **13** and **14**. In this reaction of **12**, the yield of **13** decreased and that of **14** increased considerably under an oxygen atmosphere [16], suggesting generation of thionitrosobenzene **10**. Thus, Scheme 1 may be considered to be reactions of a thionitrosobenzene intermediate.

Photolysis of the azide **17**, derived from **16**, produced the thionitrosobenzene intermediate **18** and the corresponding **13** as the main products and exhibited an absorption band at about 470 nm in an argon matrix at 12 K and in an EPA matrix in 70–80 K, indicating the existence of **18** [17]. The intermediate **18** gave the corresponding **14** and Ar–N = S = S on treatment with O_2 and thiirane, respectively [17], Scheme 1 thus being proved to be valid. Using the more bulky 2,4,6-tris[bis(trimethylsilyl)methyl]-phenyl group (this group being abbreviated as Tbt), Tbt–N = S = S was prepared [17d]. The desulfurization gave Tbt–N = S, but it could not be isolated.



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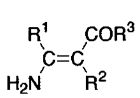

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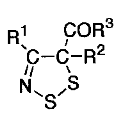

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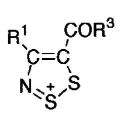

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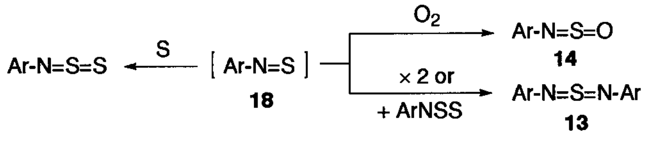
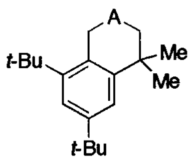
Transient *N*-thio- and *N*-selenosulfinylamines obtained from ketone hydrazones produced the corresponding thiones [18] and selones [19]. In the cases of *β*-keto enamines **19**, 5*H*-1,2,3-dithiazoles **20** were obtained, but **19** (R^2 = H) produced **20** (R^2 = OMe) in the presence of MeOH, indicating the formation of the 1,2,3-dithiazolylium salt **21** as an intermediate [20]. The latter result casts some light on the mechanism of the Herz reaction [21], which gives 6-chloro-1,2,3-benzodithiazolylium chlorides by reactions of *o*-unsubstituted anilines with S_2Cl_2. Later R. Okazaki et al. at the University of Tokyo succeeded in the preparation of telluroketones ($R^1R^2C = Te$) [22].

A sterically protected thial (Ar*CH = S) was prepared by reaction of Ar*Li with *O*-ethyl thioformate or reaction of Ar*CHO hydrazone with S_2Cl_2, as a very stable and violet crystalline compound [23,24]. It cyclized to **22** at 200°C, by irradiation, and also quantitatively by AIBN-induced reaction at 80°C [24,25]. A stable aliphatic thial $(Me_3Si)_3C$-CHS was prepared, but the reactions were complicated because of easy migration of the Me_3Si group [26]. After several attempts, a stable and blue selenal (Ar*-

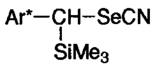


SCHEME 1

CH = Se) was prepared by reaction of **23** with n-$Bu_4N^+F^-$, but it decomposed rapidly to Ar*CHO in solutions [27]. The reactivity is greater than that of Ar*CHS, and Ar*CHSe cyclized at 70°C to **24** quantitatively analogous to **22** [27].



22 (A = S)
24 (A = Se)



$$\mathrm{Ar^*{-}\underset{\textstyle SiMe_3}{\underset{|}{C}}H{-}SeCN}$$

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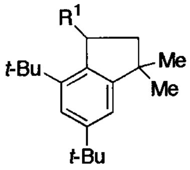

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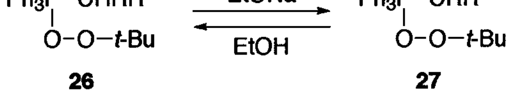
During attempts to isolate a stable sulfenic acid, a heterolytic cleavage of the C–S(O) bond was found. Oxidation of sulfides $Ar^*R^1CH\text{-}SR^2$ with MCPBA or O_3 at room temperature afforded indanes **25**, and it was proved that an intermediate sulfoxide collapsed to $Ar^*R^1CH^+$ ion [28].

NOVEL REACTIONS OF ORGANOPHOSPHORUS COMPOUNDS

Although in 1919 Staudinger reported formation of Ph_2CS by reaction of $Ph_3P = CPh_2$ with S_8, the generality of this reaction to afford ArAr′CS was confirmed in 1972 [29]. Reactions of $Ph_3P = CHR$ with NOCl gave RCN [30]. Using this method, hitherto unknown p-toluenesulfonyl cyanide was first prepared [31]. Reaction of $Ph_3P = CHPh$ with NO gave PhCHO, stilbene, and PhCN. Formation of PhCHO suggests the formation of N-nitrosoimine (PhCH = N–N = O) as an intermediate [32] (see From N-Nitrosoimines Stabilized by Heterocycles to Hypervalent Sulfur Compounds).

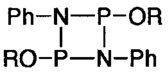
Reactions of $Ph_3P = CRR'$ with t-BuOOH and EtONa in EtOH led to an equilibrium (Scheme 2) between **26** and **27** and afforded Ph_3PO, $RR'CH_2$, $Ph_2P(O)CHRR'$, and PhH from **26** by homolysis of the O–O bond, and PhO-t-Bu, $Ph_2P(O)CHRR'$, Ph_3PO, RR′CHO-t-Bu, and RR′CHOEt were obtained from **27** via a heterolytic pathway [33].

Reactions of $Ph_3P = NAr$ with sulfenes ($RCH = SO_2$) [34] and benzenediazonium-2-carboxylate [35] to give $Ph_3P = CRSO_2NHAr$ as an initial product and 3-aryl-1,2,3-benzotriazin-4(3H)-ones, respectively, were carried out. Thermal reactions of 1,3,2,4-diazadiphosphetidines **28** with benzil or benzaldehyde, chalcone, and benzil monoanil afforded **29**, **30**, and **31**, respectively [36].



26 **27**

SCHEME 2



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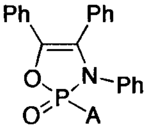
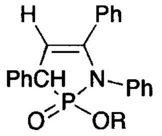


29 (A = OR)
31 (A = NHPh)



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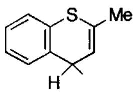
Dimethyl 1,3-benzodithiol-2-ylphosphonate was prepared from the 1,3-benzodithiolylium salt, $P(OMe)_3$, and NaI, and used in the Horner reaction [37]. Phosphonates Het-$P(O)(OMe)_2$, Het = **32**–**34**, were similarly prepared from an appropriate Het^+ salt, and the anions, prepared by treatment of the phosphonates with butyllithium, were treated with aldehydes and ketones to give the corresponding alkenes [38].

Het =



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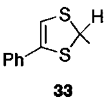

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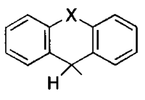
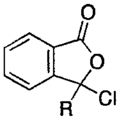


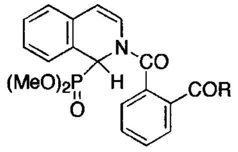
34

(X = NH, NMe, NEt, NCH_2Ph, O, S)

Dimethyl 2-isopropoxycarbonyl-1,2-dihydro-1-isoquinolylphosphonate was prepared by an initial reaction of isoquinoline with isopropyl chloroformate, and then with $P(OMe)_3$ and NaI, and the derived anion was treated with RCHO, followed by HCl in EtOH, to give 1-RCH_2-substituted isoquinolines [39]. Phosphonates **36** obtained from isoquinoline and the halide **35** afforded 13-substituted 8H-dibenzo[a,g]quinolizin-8-ones **37** by the action of i-Pr_2NLi [40]. The quinoline analog of **36** also reacted similarly [40].



35 (R = Ph, OMe, OEt, NMe_2)



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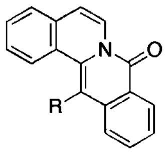

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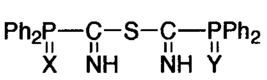
Desilylation of α-silyl phosphonates **38** with CsF, followed by treatment with R^1R^2CO, afforded $R^1R^2C = CHR$ [41], and reactions of β-hydroxy phosphonates **39**, prepared from $(MeO)_2P(O)CH_2Li$ and R^1R^2CO, with CsF-H_2O (1:1) produced $CH_2 = CR^1R^2$ [43], the presence of H_2O being indispensable. Similar Horner-Emmons reactions have been reported independently by Bestmann et al. [42]. Analogously, β-hydroxy phosphonates **40** produced $R^3CH = CR^1R^2$

with K_2CO_3-H_2O (1:1), although the reaction did not occur with a strong base such as NaH or *t*-BuOK [43b,44]. Dehydration of **39** and **40** with carbodiimide also produced alkenes through oxaphosphetane intermediates [44b]. T. Kawashima (University of Tokyo) has investigated the Wittig and related reactions using Martin's ligand.

$Me_3SiCHR{-}P(O)(OMe)_2$ $\qquad$ $(MeO)_2P(O)CHR{-}CR^1R^2{-}OH$

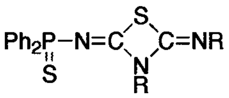
38 $\qquad$ **39** (R = H), **40** (R = R^3)

It is well known that Ph_2NCSNH_2 is produced by the reaction of Ph_2NH with NH_4SCN in the presence of HCl gas, but the phosphorus analog Ph_2PH gave **41** under similar conditions. Similarly, $Ph_2P(O)H$ produced **42** and $Ph_2P(S)NCS$ [45]. The expected compound Ph_2PCSNH_2 was obtained by reaction of Ph_2PH with HSCN in ether [45]. Cycloaddition of $Ph_2P(S)NCS$ with carbodiimide gave the 1,3-thiazetidine **43** [46].



$\underset{\underset{X}{\|}}{Ph_2P}-\underset{\underset{NH}{\|}}{C}-S-\underset{\underset{NH}{\|}}{C}-\underset{\underset{Y}{\|}}{PPh_2}$

41 (X, Y = O, S)
42 (X = O, Y = O, S)



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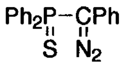
Reactions of ambident reagents $[Ph_2PX]M$ (X = O, S; M = Li, Na, MgCl, ZnCl, FeCl) with alkyl halides, aldehydes, ketones, *p*-benzoquinone, and tetrahydrofuran (THF) took place at the P atom [47–50], but the reaction products depended on the nature of M. The structures of $[Ph_2PX]M$ were shown to be $Ph_2P{-}X{-}M$ by comparison of their Raman spectra and ^{31}P data with related compounds [51]. Moreover, it was found that the species $[Ph_2PS]M$ easily disproportionates to $Ph_2P(S)SM$ and Ph_2PM.

Tetraphenyldiphosphane was found to undergo $S_H2(P)$ attack on the P–P bond by carbon radicals [52]. Diphosphane *P*, *P′*-dioxides and *P*, *P′*-disulfides undergo insertion of O and S atoms into the P–P bond by the action of perbenzoic acid (at 0°C) and S_8 (at 160°C), the latter being attributable to homolysis of the P–P bond. Thus, the observation that diphosphane *P,P′*-disulfides when heated at 140–180°C under an oxygen atmosphere produced the corresponding anhydride, supports the homolysis concept [53].

Phenyldithiophosphinates, $Ph_2P(S)SR$, reacted with R′Li by an $S_N2(S)$ pathway to give sulfides RSR′ but did not react with Grignard reagents [54]. This reaction was applied to the synthesis of sulfides, and other product, $[Ph_2PS]Li$, was recycled to the starting esters [55]. This method was not affected by the presence of ester, amide, carbonyl, cyano, and chloro groups in the substrate [56]. This method could be applied to the synthesis of unsymmetrical disulfides RSSR′ using both R′SLi and an equimolar amount of S_8 in THF-HMPA solution [56], where S_8 suppresses further reaction between the disulfide and $[Ph_2PS]Li$ owing to conversion of the lithium reagent to $Ph_2P(S)SLi$.

An intriguing 1,2-sulfur shift has been found. The α-diazo phosphine sulfide **44**, which was first prepared by us, afforded the rearranged products **45** by reactions with acetic acid (r.t.), H_2O (hν or heat), and MeOH (hν), the intermediate being considered to be either **46** or the protonated phosphonium ion [57].



$\underset{\underset{S}{\|}}{Ph_2P}-\underset{\underset{N_2}{\|}}{CPh}$

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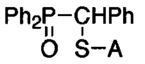
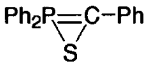


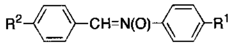
$\underset{\underset{O}{\|}}{Ph_2P}-\underset{\underset{S-A}{|}}{CHPh}$

45 (A = $COCH_3$, H, CH_3)



46

It was found that mixing of equimolar amounts of phenylthiophosphonic dichloride (r.t., 0.5 d) and *O*-methyl diphenylthiophosphinate (150°C, 1–2 d) brought about cyclization reactions to give α,*N*-diarylnitrones **47** to **48** (A = S, O), respectively, and the mechanisms were studied [58]. The latter reaction involves homolysis of the intermediate **49**, and, when oxygen (or air) was present, $Ph_2P(S)OMe$ was sufficient in only a 0.1 molar amount. Furthermore, diphenylthiophosphinic acid was found to be an efficient catalyst for the reaction.



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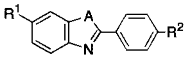
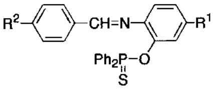
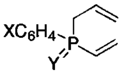


48 (A = S, O)



49

Phospha-Cope rearrangements of **50** and **52** produced **51** and **53**, respectively, in the presence of alcohol (ROH) [59,60]. In the reaction of **50**, the effect of the X group on the reaction rate showed a positive ρ value in the Hammett equation, and the Y atom accelerated the rearrangement in the following order: O < S < Se.



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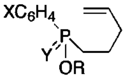

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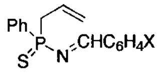

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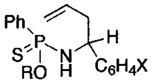
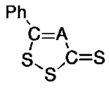


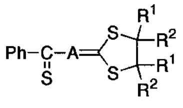
53

FROM REACTION OF S ATOM TO STABILIZATION OF o-THIOQUINONEMETHIDES

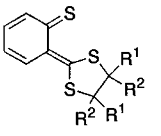
In order to investigate the reactivity of the S atom, 5-phenyl-1,2,3,4-thiatriazole was photolyzed in the presence of cyclohexene to give cyclohexene episulfide, but the yield was below 10% [61]. Then, other analogous heterocycles were examined. Unexpectedly, photolyses of **54** and **55** in the presence of a (cyclo)alkene produced colored compounds **56** and **57**, respectively, this arising from the triplet state of the heterocycle [62–64]. The cycloaddition reactions to **56** and **57** have also been studied [65–67].



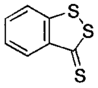
54 (A = N)
55 (A = CR)



56 (A = N)
57 (A = CR)

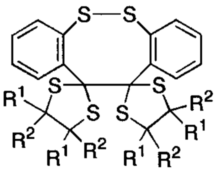


58



59

By application of the previous reaction, a reactive intermediate, *o*-thioquinonemethide **58**, was expected to be produced. In fact, photolysis of **59** in the presence of a (cyclo)alkene afforded the expected **58** as a deep blue solution, but the isolated crystals were a colorless, head-to-head [4 + 4] dimer **60** [68]. Independently, de Mayo et al. reported a similar result [69]. The structure of **60** ($R^1 = R^2 = Me$) was finally determined by isolation of the isomeric head-to-tail [4 + 4] dimer **62** by reaction of **58** ($R^1 = R^2 = Me$) with the enamine **61** and by comparison of the ^1H NMR data of the methyl signals. The dimer **62** did not dissociate to the monomer in solutions [70]. Cycloaddition reactions for **58** have been carried out [68,71].



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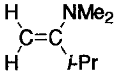
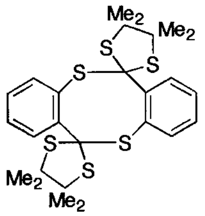
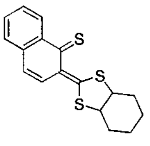


61

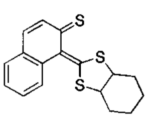


62

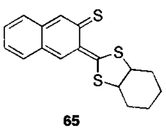
In order to stabilize the *o*-thioquinonemethide structure, the naphtho analogues **63**, **64**, and **65** were prepared from naphtho[2,1-, 1,2-, and 2,3-*d*]-1,2-dithiole-3-thiones, respectively [72]. The compound **63** was a monomer, **64** showed an equilibrium with the [4 + 2] dimer, and **65** existed only as a dimer **66** because of less aromaticity in the monomer **65**. These compounds **63**, **64**, and **66** underwent cycloaddition reactions.



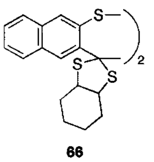
63



64

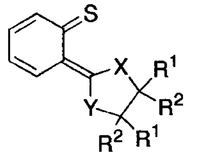


65

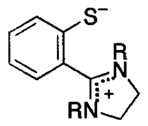


66

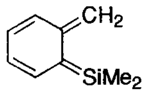
In order to compare their properties, compounds **67**, **68**, and **69** were prepared. Compound **67** existed as a polar form **70**, and **68** and **69** existed in an equilibrium with the dimer in solutions [73].



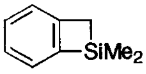
67 (X = Y = NR)
68 (X = Y = O)
69 (X = S, Y = O)



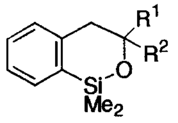
70



71



72



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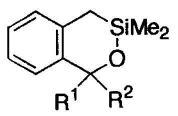
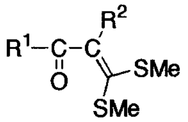


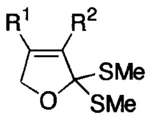
74

In connection with these results, in order to examine a possibility of the existence of the *o*-quinonoid intermediate **71**, 1,2-dihydro-1-benzosilete **72** was photolyzed in the presence of ketones. As a result, 1*H*-3,4-dihydro-2,1-benzoxasilins **73** were isolated, along with the isomer **74** only in the cases of acetone and 2-butanone [74]. Therefore, this reaction is the first example of an $S_H2(Si)$ attack on the Si–C bond by the triplet state of a ketone without formation of **71**.

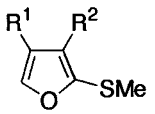
Acylketene dithioacetals **75** reacted with methylenedimethylsulfurane to give 2,2-bis(methylthio)-2,5-dihydrofurans **76** which were transformed into 2-(methylthio)furans **77** in a Florisil column in the presence of a catalytic amount of acid [75]. From **76** and **77**, various types of furan derivatives were prepared.



75



76

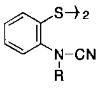


77

FROM N-NITROSOIMINES STABILIZED BY HETEROCYCLES TO HYPERVALENT SULFUR COMPOUNDS

The existence of an *N*-nitrosoimine was assumed (Novel Reactions of Organophosphorus Compounds) [32]. *N*-Nitrosoimines stabilized by heterocycles have been reported, such as 2-nitrosoimino-2,3-dihydrobenzothiazole **78**, which thermally decomposed to the corresponding 2-one [76]. The resonance (Scheme 3) for **78** was indicated by means of ESCA and ^1H NMR ($R = Me$) spectra by comparison with the corresponding data of related compounds [77].

Photolyses of **78** and the analogs were carried out. In the case of **78**, disulfides **79** were obtained as a main product through *π*–*π** excitation [78]. Similarly, the *N*-nitrosoimine of Hector's base **80** gave **81** as a main product, which exhibited an abnormally high $\nu_{C=N}$ value (1660 cm^{-1}), and **81** was also obtained by reaction of Hector's base with PhNHCN, which was a decomposition product of **80** [79]. The structure of **81** was confirmed, using the compound containing three *p*-bromophenyl groups instead of three phenyl groups, by X-ray crystallography [80]. The high $\nu_{C=N}$ value is attributed to the short bond length (128 pm) of the side chain C = N bond in **81a** and the N···S bond length (253.8 pm) in **81a** is shorter than the sum (335 pm) of the van der Waals radii of S and N atoms, indicating an interaction between the N and S atoms [80]. An intermediate for the formation of **81** is considered to be a hypervalent sulfur compound **82** [80]. From comparison of the ^{13}C NMR data with those of related compounds, the N···S interaction was attributed to an electron transfer from the N atom to the S atom [81].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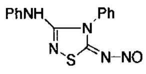
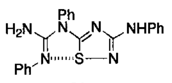
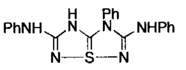
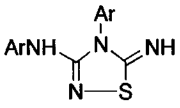
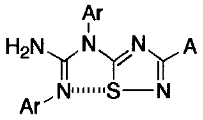

80

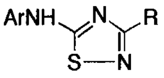

81
81a (Ph ⇒ *p*-BrC$_6$H$_4$)


82

Generally, Hector's base analogs **83** afforded addition-rearrangement products **84** and **85** with Ar′NHCN and nitriles (RCN) or imidates [RC(= NH) OEt], respectively, and the thermolysis of **85** gave **86** by elimination of ArNHCN [82].

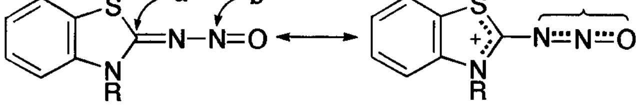

83


84 (A = NHAr′)
85 (A = R)


86

Reactions of **83** with activated acetylenes gave addition-elimination products **87** and ArNHCN [83,84]. Generally the following addition-elimination reactions (Scheme 4) took place.

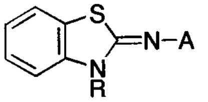
These studies were developed into extensive examinations of hypervalent chemistry by K.-y. Akiba (now Professor Emeritus) and Y. Yamamoto at Hiroshima University.

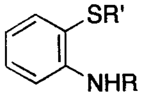


SCHEME 3

Let us now turn to the topic of *N*-nitrosoimines. The nitrosoimine **78** was allowed to react with Grignard reagents (R′MgX), because **78** is an ambident electrophile as shown in Scheme 3 [85]. Using ArMgBr, **88** (R′ = Ar) was obtained, along with **89** (R′ = Ar) (*a* attack > *b* attack). In the cases of bulky R′ groups (R′ = mesityl (Mes), *t*-Bu) **90** was produced instead of **88** (also *a* > *b*). With PhCH$_2$MgCl **91** was isolated in a much larger ratio than with **88** (R′ = PhCH$_2$) (*b* ≫ *a*), and with aliphatic Grignard reagents the reactions were complex, but *b* attack is more prevalent than *a* attack. In the cases of organolithiums (R′Li), the main pathway was *c* attack to give **92** (R′ = Ph, *n*-Bu, PhCH$_2$) (*c* >>> *a*, *b*) [86].


88 (X = R′)
90 (X = H)

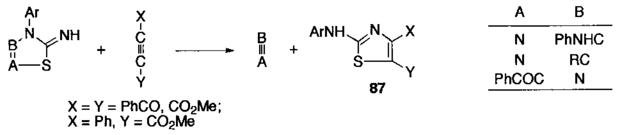

89 (A = NHR′)
91 (A = PhCH=N–)


92

Further the following results (*a* attack) were found (Schemes 5 and 6) [87].

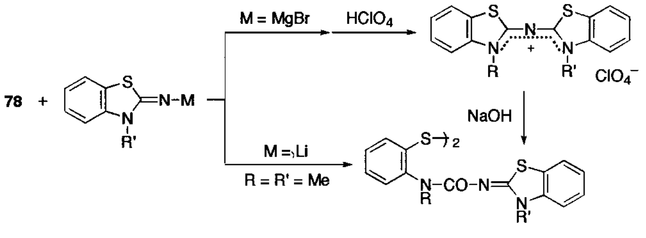
Studies on *N*-nitrosoimines have been summarized in a review article [88].

The reaction (Scheme 7) afforded a novel rearranged product **95** through *a* attack on **93**. However,

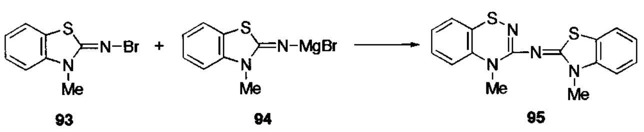


A	B
N	PhNHC
N	RC
PhCOC	N

SCHEME 4



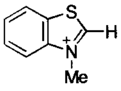
SCHEME 5 and 6

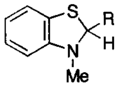


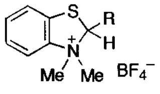
SCHEME 7

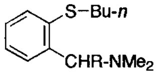
no 3-phenyl derivative of **94** gave an analogous rearranged product because of the following equilibrium (Scheme 8) in **94a** [89].

Reactions of the benzothiazolium salt **96** with Grignard reagents (RMgX) gave **97** [90], which were methylated on the N atom by use of the Meerwein reagent ($Me_3O^+BF_4^-$) to yield 2,3-dihydrobenzothiazolium salts **98** [91,92].


96


97


98

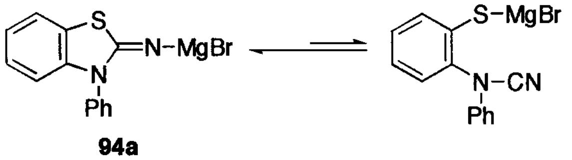

99

The salt **98** afforded the rearranged product **99**, butyl phenyl sulfide, and *o*-butylthio-*N,N*-dimethylaniline with butyllithium, indicating the attack on S and the unusually high migratory aptitude of the *o*-(butylthio)phenyl group [92,93]. The latter result was supported by the independent reaction shown in Scheme 9.

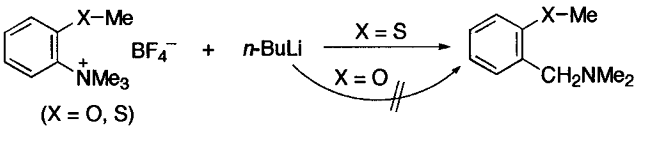
FROM PHOSPHINIDENES (R–P) TO KINETIC STABILIZATION OF LOW COORDINATED ORGANOPHOSPHORUS COMPOUNDS

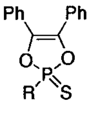
In 1965 (a full article in 1968) Schmidt et al. reported the generation and reactions of a phosphorus analog of nitrenes, phosphinidenes (R–P) [94]. Since phosphorus is in the third period, phosphinylidenes (R–P = O) and phosphinothioylidenes (R–P = S), analogous to nitroso and thionitroso compounds, are considered to exist as reactive intermediates.

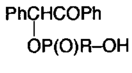
In fact, these intermediates were generated by the reactions of phosphonic and thiophosphonic dichlorides with Mg and analogously trapped with diethyl disulfide and benzil to give $RP(X)(SEt)_2$ (X = O, S) and the adduct **100** (in X = O, hydrolyzed product **101**), respectively. The species Ph–P = S gave a [4 + 2] cycloadduct **102** with 1,3-butadienes, but the species Ph–P = O formed a [4 + 1] cyclo-adduct **103** [95]. However, reaction of Ph–P = S with 2,3-diphenyl-1,3-butadiene produced the adduct **104**. This fact is attributed to the existence of the equilibrium (Scheme 10) by a separate experiment [96] using **105** as the generator [97].


94a

SCHEME 8


SCHEME 9


100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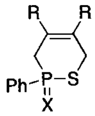
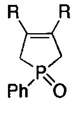
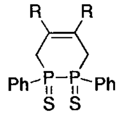
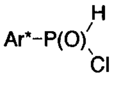

102 (X = O, S)


103


104 (R = Ph)
105 (R = H)

Considering the fact that Ar*N = O exists only as a monomer (see From Novel Radical Reactions to Kinetic Stabilization of Organosulfur and Selenium Compounds), it is expected that the species Ar*–P = X (X = O, S) may be stabilized by steric protection or kinetic stabilization. Then, the compound **106**, reported in the literature [98], was expected to be a generator of Ar*–P = O by the α-elimination of HCl. However, it was found that the true structure of **106** was **107** [99]. Next, in expectation of the formation of $Ar^*–P(O)Cl_2$, the reaction of Ar*–Li with $POCl_3$ was carried out, but, unexpectedly, the product was a very crowded compound **108** [100]. To my surprise, a large optical rotation was observed in the single crystal, indicating a natural optical resolution during the production of the single crystals and the presence of an asymmetric phosphorus atom, in spite of the presence of two identical Ar* groups. The chirality results from the different deformation angle (17.8° and 19.1°) of the two Ar* groups in the boat form [101].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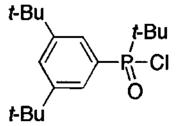
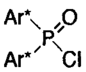
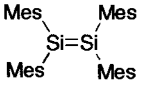

107


108


110

On the expectation of the isolation of Ar*–P, the reaction of Ar^*PCl_2, prepared from Ar*Li and PCl_3, with Mg, was performed, but, unexpectedly and surprisingly, a diphosphene or so-called phosphobenzene, (*E*)-Ar*–P = P–Ar* **109** was obtained in the form of a very stable orange-red crystals [102]. Al-


SCHEME 10

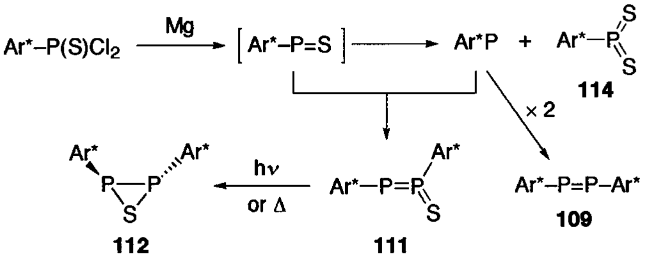
though formation of phosphobenzene Ph–P = P–Ph has been reported in 1877, the true structure has been proved to be $(\mathrm{Ph\text{-}P})_{3\text{–}6}$. Therefore, true diphosphenes had been thought to be unstable compounds before 1980. From these facts, a so-called double-bond rule was proposed in 1979 [103]. The rule states that the multiple bond between higher period elements is very weak and such unsaturated compounds are too unstable to exist as stable compounds. West et al. also reported isolation of a stable tetramesityldisilene **110** at a later time [104]. Thus the rule was invalidated and overthrown.

Stable unsymmetrical diphosphenes (*E*)–Ar*–P = P–Ar (Ar = Mes, 2,4-$(t\text{-Bu})_2$-6-$\mathrm{MeC_6H_2}$) were prepared by reaction of $\mathrm{ArPCl_2}$ with air-insensitive but stable $\mathrm{Ar^*PH_2}$, obtained by reduction of $\mathrm{Ar^*PCl_2}$ with $\mathrm{LiAlH_4}$, in the presence of DBU. However, in the case of Ar = Ph, the corresponding diphosphene was stable only in solutions [105].

Reactions of $\mathrm{Ar^*PH_2}$ with $\mathrm{H_2O_2}$ or $\mathrm{S_8}$ yielded stable $\mathrm{Ar^*P(O)H_2}$ or $\mathrm{Ar^*P(S)H_2}$, respectively [106]. Diphosphene **109** quantitatively gave $\mathrm{Ar^*P(O)Cl_2}$ (independent of solvent), Ar*Br (in $\mathrm{CCl_4}$) or $\mathrm{Ar^*P(O)Br_2}$ (in MeOH-$\mathrm{CCl_4}$), and Ar*H (independent of solvent) with $\mathrm{Cl_2}$, $\mathrm{Br_2}$, and $\mathrm{I_2}$, respectively [107], and an addition product with *n*-BuLi [108].

Diphosphene **109** gave a sulfide Ar*–P(S) = P–Ar* **111** with $\mathrm{S_8}$, and **111** was quantitatively converted to thiadiphosphirane **112** by heating or irradiation [109]. The isomerization was supported by the results of an MO calculation [110]. The diphosphene Ar*–P = P–Ar behaved similarly, except for sulfurization on the less hindered P atom closing to an Ar group [111]. Reaction of $\mathrm{Ar^*P(S)Cl_2}$ with Mg did not give a stable Ar*–P = S, but gave the further reaction products as shown in Scheme 11 based on ^{31}P NMR spectroscopy [113].

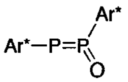
Oxidation of **109** with MCPBA did not give the monooxide **113** analogous to azoxybenzene, but rather the decomposition products produced by *m*-chlorobenzoic acid and moisture [112]. However, reaction of $\mathrm{Ar^*P(O)Cl_2}$ with Mg produced a very moisture-sensitive but thermally stable diphosphene P-oxide **113**, although the isolation was very troublesome [112], but stable Ar*–P = O was not detected.



SCHEME 11

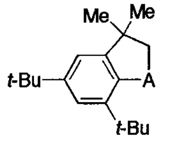
Reaction of **109** with Se–$\mathrm{Et_3N}$ afforded the selenium analogs of **112** and **114** [114]. The diphosphene **109** was reduced to Ar*PHPHAr* with $\mathrm{LiAlH_4}$ or Vitride $[\mathrm{Na(MeOCH_2CH_2O)_2AlH_2}]$ [115].

The phosphine $\mathrm{Ar^*PH_2}$ produced the very stable dithioxophosphorane **114** by sulfurization with $\mathrm{S_8}$ and 2,6-lutidine [116]. The synthesis of **114** was reported independently from several laboratories.



$\mathrm{Ar^*{-}P{=}\overset{Ar^*}{\underset{O}{P}}}$

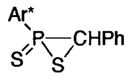
113



115 (A = P(S)Cl)
116 (A = PH)

Ar*–P=CHPh

117



118

An attempt to prepare $\mathrm{Ar^*P(S)Cl_2}$ by reaction of $\mathrm{Ar^*PCl_2}$ with $\mathrm{PSCl_3}$ or $\mathrm{S_8}$ at 110°C yielded an intramolecular cyclization product (phosphaindane) **115**. The cyclization was proved to occur with $\mathrm{Ar^*PCl_2}$ [117]. The diphosphene **109** gave the phosphaindane derivative **116** by photolysis without use of a filter, indicating the formation of a free Ar*–P as an intermediate [118]. Since no **116** was obtained in the formation of **109** [102], the intermediate is considered to be, not free Ar*–P, but rather phosphinidenoid Ar*PCl–MgCl.

Although the stable phosphaalkene Mes–P = $\mathrm{CPh_2}$ was first isolated by F. Bickelhaupt et al. in 1978 [119], we prepared (*E*)-**117**, which gave an equilibrium mixture with the *Z*-isomer by irradiation. The sulfurization of **117** gave thiaphosphirane sulfide **118** [120]. Various phosphacumulenes **119**–**123** were synthesized as shown in Scheme 12.

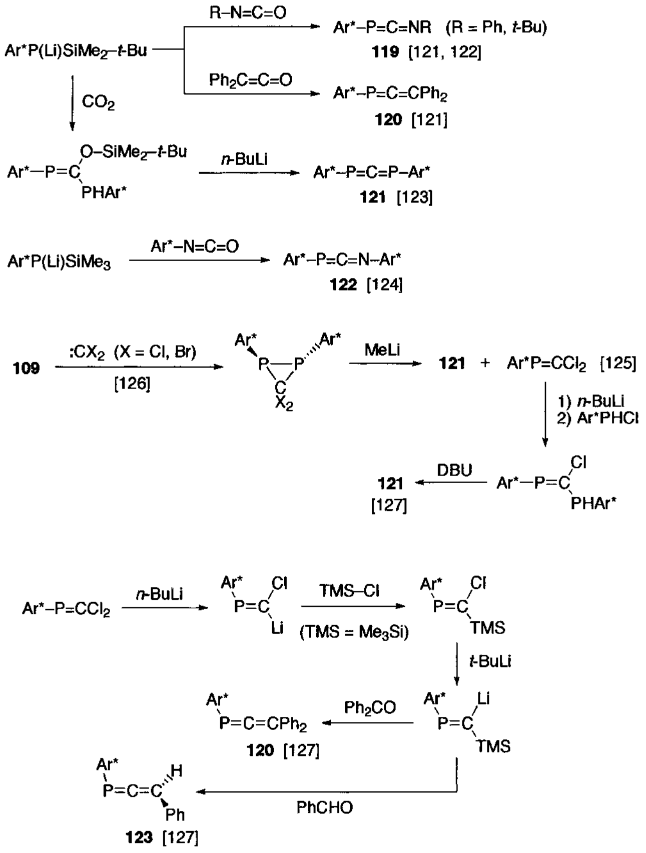
1-Phosphaallenes **119** and **122** showed a large contribution of the canonical form **119a** based on ^{13}C and ^{31}P NMR data, X-ray crystallography, and the result of hydrolysis.

$$\mathrm{Ar^*{-}P{=}C{=}N{-}R} \longleftrightarrow \mathrm{Ar^*{-}\overset{-}{P}{-}C{\equiv}\overset{+}{N}{-}R}$$

119 **119a**

Since 1,3-diphosphaallene **121** is axially dissymmetric, **121** was resolved using a chiral HPLC column, and the (*R*)-(−)-isomer was isolated in pure form. The isomer is stable in the dark but is completely racemized by 3 minutes of irradiation [128]. Later, 1-phosphaallene **123** was also resolved using a chiral column by M. Yoshifuji et al. of Tohoku University and also racemized by irradiation [129].

The corresponding diphosphenes and 1,3-diphosphaallenes were also prepared in the stable



SCHEME 12

form using 2,6-di-*tert*-butylphenyl and 2,4,6-tri-*tert*-pentylphenyl groups as a protecting group instead of the Ar* group [130,131].

An attempt to prepare Ar*–P=C: from (*E*)-**124** Ar*P=CHCl and *t*-BuLi unexpectedly led to the phosphaalkyne Ar*–CP, but (*Z*)-**124** did not give Ar*CP by the same treatment [132].

Further development of low coordinated phosphorus chemistry has been carried out by M. Yoshifuji at Tohoku University. Using the more bulky Tbt group, R. Okazaki (now at Japan Women's University) and N. Tokitoh (now at Kyoto University) at the University of Tokyo, after my retirement, stabilized low coordinated heteroatom compounds containing group 14 elements.

As one of the other themes, benzocyclopropene produced photochemically 1,6-diiodo- or -bis(thiocyanato)-1,3,5-cycloheptatriene with I_2 or $(SCN)_2$, respectively, and from the products S-containing macrocycles were derived [133].

Our major studies on heteroatom chemistry have been outlined briefly. Especially, kinetic stabilization is suitable to examine physical properties without any perturbation from electronic effects, but a demerit is the remarkable decrease of the reactivity as a matter of course. Because there are many heteroatoms, our studies are only the first stage in a journey to heteroatom chemistry. Further development and application of this field are earnestly desired.

I wish to express my thanks to all coworkers including skillful and hardworking staffs and students. I also thank Dr. A. Ishii, Saitama University, for preparation of chemical structures.

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