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Reactions of α-Diketones and *o*-Quinones with Phosphorus Compounds

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I. Introduction

The chemistry of organic phosphorus compounds has shown a remarkable growth throughout the past 5 decades. Meanwhile, it has attracted much interest, especially the extensive utilization of the organophosphorus derivatives as plasticizers for synthetics, as extraction agents, as oxidation inhibitors for lubricants, as flotation agents, as complexing agents for transition metals, and as insectisides.[1−3] This variety is due to the ability of phosphorus to occur in a large number of different valence and coordination states.

The electronic structure of phosphorus consists of 15 electrons in the ground-state distributed as $1s^2 2s^2 2p^6 3s^2 3p_x^1 3p_y^1 3p_z^1$. This distribution and the relevant orbital energies lead to well-defined families of tri-, tetra-, penta-, and hexacoordinate derivatives in which the ligands can be organic or inorganic.

The phosphorus atom forms many types of compounds. Some of the general types with the orbitals used in the formation of the bonds and their geometry are shown in Table 1.[4−6]

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Fayez H. Osman was born in 1938 in Cairo, Egypt. He graduated from the University of Cairo with a B.Sc. in chemistry and physics. He was awarded a M.Sc. in 1970 and a Ph.D. in 1973 from the same university in organophosphorus chemistry. He held the following positions at the National Research Centre in Cairo: Research Scholarship (1965–1967), Research Assistant (1967–1973), Researcher (1973–1978), Research Associate Professor (1978–1985), Research Professor (1985–1998), and Emeritus Professor (since 1998). He participated in and supervised research projects in the field of organophosphorus chemistry. He was granted research fellowships and short visits to the Université Paul Sabatier, Laboratoire des Heterocycles du Phosphore et de l'Azote au CNRS, Toulouse, France (1976–1978, 1979); the Centre of Molecular and Macromolecular Studies, Łodz, Poland (1980); and the University of Massachusetts, Department of Chemistry, Amherst, Massachusetts (1986–1987).

Fatma A. El-Samahy was born in 1961 in Menoufia, Egypt. She graduated from the University of Menoufia with a B.Sc. in chemistry. She was awarded a M.Sc. in 1994 and a Ph.D. in 2000 from the University of Cairo. She joined the National Research Centre in Cairo as a Research Assistant under the supervision of Professor F. H. Osman in 1989 and now holds the position of Researcher. Her research work is mainly focused on the behavior of some phosphorus reagents toward certain carbonyl compounds.

The direct synthesis of organic phosphorus compounds from elemental phosphorus has attracted

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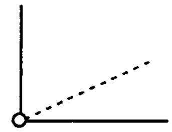
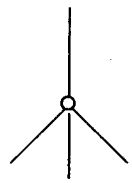
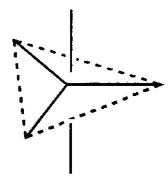
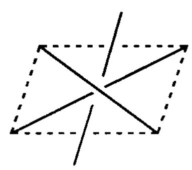
Table 1

Number of bonds or valency	Orbital or hybrid	Directional properties and Geometry		Example
3	*p* (Lone pair present)		pyramidal	PH_3
4	sp^3	 (in compounds with PO and PS bond *d* orbitals of phosphorus may be used in $d\pi$ - $p\pi$ bonding)	tetrahedral	PH_4^+ $OP(OH)_3$, $POCl_3$
5	sp^3d		trigonal bipyramid	PCl_5, PF_5
6	sp^3d^2		octahedral	PF_6^-

great interest, and it is possible to prepare a wide variety of organophophorus compounds.[7]

The Wittig reaction, which converts an aldehyde or ketone into an olefin by its reaction with phosphonium ylides,[8−13] opened up a new field of organophosphorus chemistry. Also, the optically active phosphines prepared by Horner and co-workers[14,15] greatly stimulated the entire field of phosphine chemistry.

The alkyl esters of phosphorus acid are classified into three groups: primary [$ROP(OH)_2$], secondary [$(RO)_2POH$], and tertiary [$(RO)_3P$]. The latter two groups are the most important and reactive ones. The dialkyl esters, however, show a little of the nucleophilicity exhibited by the trialkyl esters. This is apparently due to the presence of phosphorus atom in the pentavalent rather in the trivalent state. The reaction of trivalent phosphorus reagents with carbonyl compounds assumed much greater synthetic value when Ramirez et al.[16−29] discovered that the adducts are capable of reacting further with a variety of carbonyl compounds producing new carbon−carbon bonds under very mild and neutral conditions.

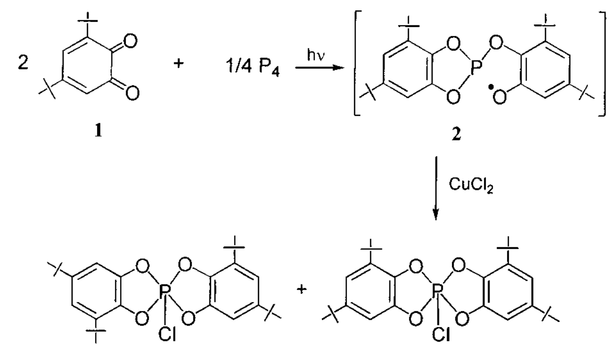
The phosphorus accompanied by thiyl transfer, such as with Lawesson's reagent,[30] converts ketones into thioketones,[31] amides into thioamides,[32] and esters into the corresponding thionoesters.[33]

The scope of this review is a survey of the reactions of α-diketones and *o*-quinones with phosphorus compounds, since these types of α-dicarbonyls exhibit different reactivities, depending on the substituent groups. Also, this review will throw light on the importance of organophosphorus compounds in organic and bio-organic chemistry.

II. Reactions with Elemental Phosphorus

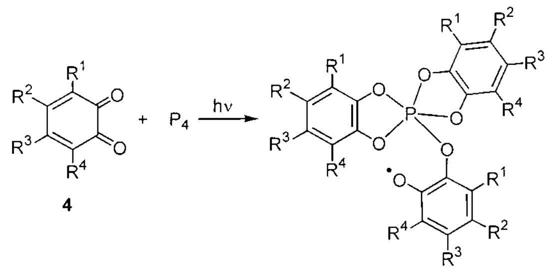
The photochemical reactions of *o*-quinones with elemental phosphorus has been studied by Kabachnik.[34] Irradiation of a mixture of 3,5-di-*tert*-butyl-*o*-quinone (**1**) and white phosphorus in benzene at 35 °C in the presence of anhydrous $CuCl_2$ leads to the formation of chlorophosphorane as a mixture of two isomers, **3A** and **3B**, through the radical intermediate **2**. This isomerization is due to a square pyramidal configuration. Accordingly, its ^{31}P NMR chemical shift gives two signals.[35,36]

The irradiation of a mixture containing the substituted *o*-quinones **4** [$R^1 = R^3 =$ *t*-Bu, $R^2 = R^4 =$ H; $R^1 = R^4 =$ *t*-Bu, $R^2 = R^3 =$ H; $R^1R^2 = R^3R^4 = (CH)_4$; $R^1 = R^2 = R^3 = R^4 =$ Cl; $R^1 = R^2 = R^4 =$ H, $R^3 =$



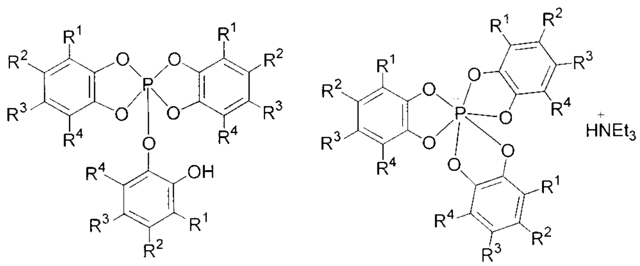
1 2 3A 3B

CPh$_3$] and white phosphorus in toluene or diethyl ether yields the free radical **5** as shown by ESR.[37,38]



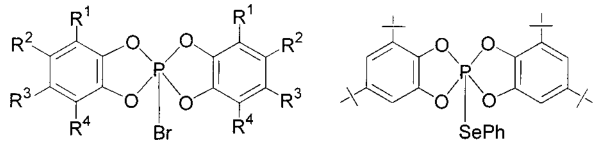
4 5

When the above reaction was carried out in the presence of the corresponding pyrocatechols, the oxyspirophosphoranes **6** were formed in high yields. Treatment of **6** with triethylamine gave the hexacoordinate phosphorates **7**. The isomerism of certain products was identified by ^{31}P NMR.[39,40]



6 7

The oxidation of white phosphorus by substituted *o*-benzoquinones **4** ($R^1 = R^2 = R^3 = R^4$ = Cl, Br; $R^1 = R^3$ = *t*-Bu, $R^2 = R^4$ = H) in the presence of bromine forms the bromophosphoranes **8**.[41] Also, it has been



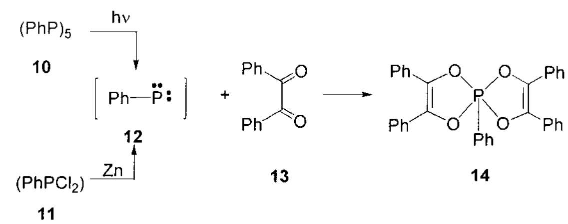
8 9

reported that 3,5-di-*tert*-butyl-*o*-quinone **1** does not react with white phosphorus and Ph_2Se_2, but in the presence of catalytic quantities of bromine the reactants produce the phosphorane **9**.[41] The ESR spectra identified the presence of the corresponding *o*-semiquinone species of these reactions. The ^{13}C and ^{31}P NMR spectra of these phosphoranes are reported.[41]

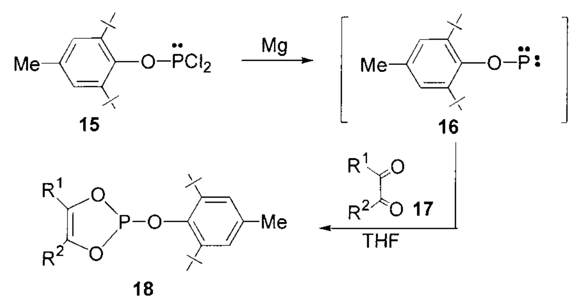
III. Reactions with Low-Coordinated Phosphorus Intermediates

Phosphinidenes (R−P̈:),[42,43] phosphinidene oxides (R−P̈=O),[44] and phosphinidene sulfides (R−P̈=S)[45−47] have been proposed as reactive species derived by the reaction of their corresponding dichlorides with magnesium or zinc metal. These low-coordinated phosphorus compounds are postulated as intermediates in the formation of 1,3,2-dioxaphospholenes by their reactions with α-diketones[43−48] and *o*-quinones.[48−50]

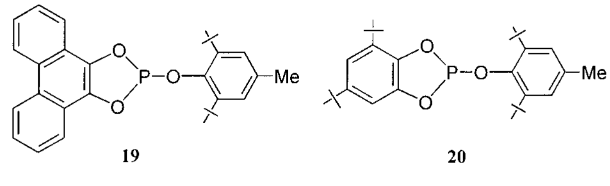
Schmidt et al.[43] have reported that the reaction of benzil (**13**) with phenylphosphinidene (**12**) generated by photochemical decomposition of pentaphenylcyclopentaphosphane (**10**) or by thermal dechlorination of phenylphosphonous dichloride (**11**) with zinc gives 2,3,5,7,8-pentaphenyl-1,4,6,9-tetraoxa-5-phosphaspiro-[4.4]nonadiene (**14**).[43]



On the other hand, Chasar[48] found that aryloxyphosphinidenes **16** can be generated by the reaction of 2,4-di-*tert*-butyl-4-methylphenylphosphorodichloridite (**15**)[51] with magnesium and then trapped by substituted α-diketones **17** (R^1 = Ph, R^2 = Me; $R^1 = R^2$ = Ph; $R^1 = R^2$ = *p*-MePh; $R^1 = R^2$ = *p*-MeOPh) in tetrahydrofuran to give 1,3,2-dioxaphospholenes **18**.[48]

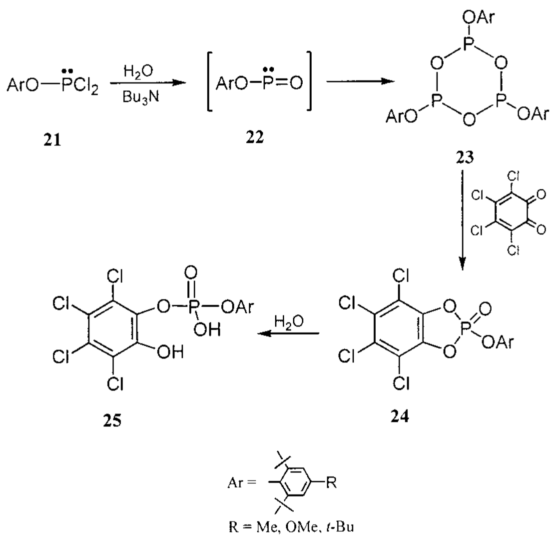


Similarly, by the same procedure, phenanthrenequinone and 3,5-di-*tert*-butyl-*o*-benzoquinone react with the phosphinidene **16** to form the corresponding products **19** and **20**, respectively.[48] These reactions are good evidence for the existence of the monocoordinate aryloxyphosphinidene intermediate (RO−P̈:).



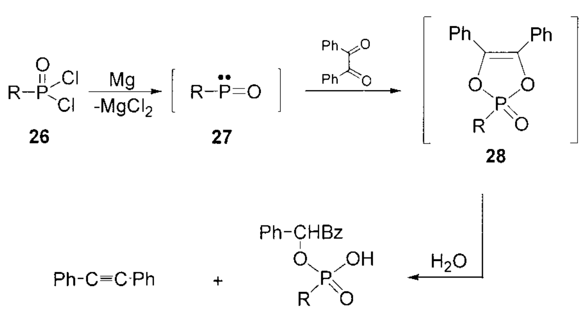
19 20

Phosphinidene oxides and phosphinidene sulfides as dicoordinated phosphorus compounds would be expected to behave similarly as phosphinidenes. In 1986, it was demonstrated by Chasar and co-workers[52] that phosphorodichloridites **21** with sterically demanding *O*-aryl groups could be controlled by partial hydrolysis to give 1,3,5,2,4,6-trioxatriphosphorinane derivatives **23**, via the phosphinidene oxides **22**. The trimer **23** reacts quite readily with 3 equiv of tetrachloro-1,2-benzoquinone in chloroform at room temperature to form the cyclic phosphate **24**, which with water gives the ring-opened product **25**.[53]



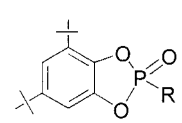
21 **22** **23** **24** **25**

When phosphonic dichlorides **26** (R = Ph, cyclo-C_6H_{11}) are dechlorinated with a slight excess of magnesium in the presence of benzil, they give the α-benzoylbenzyl phosphonates **29**, derived from 1,3,2-dioxaphosphole 2-oxides **28**, together with a considerable amount of diphenylacetylene.[45]



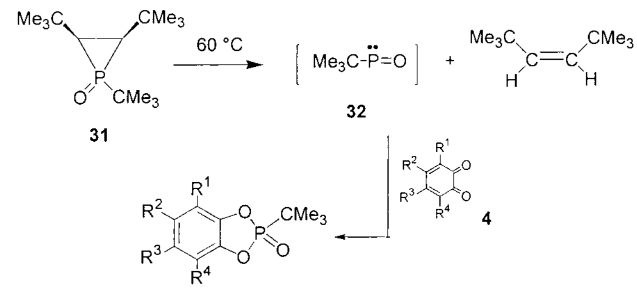
26 **27** **28** **29**

However, the reaction of phosphinidene oxides intermediate **27** (R = NMe_2, *t*-Bu) with 3,5-di-*tert*-butyl-*o*-benzoquinone in toluene-d_8 or benzene-d_6 led to the formation of 1,3,2-dioxaphosphole 2-oxides **30**.[49,50]



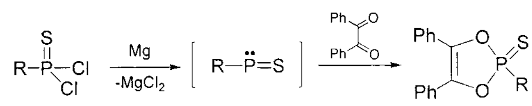
30

The unstable *tert*-butylphosphinidene oxide (**32**) can be detected when the thermolysis of the *cis*-1,2,3-tri-*tert*-butylphosphirane oxide (**31**) is carried out in the presence of 9,10-phenanthrenequinone [**4**, $R^1R^2 = R^3R^4 = (CH)_4$] and 3,5-di-*tert*-butyl-*o*-benzoquinone (**4**, $R^1 = R^3 = t$-Bu, $R^2 = R^4 = H$) in benzene-d_6 to yield a quantitative yield of 1,3,2-dioxaphosphole 2-oxide **33**.[54]



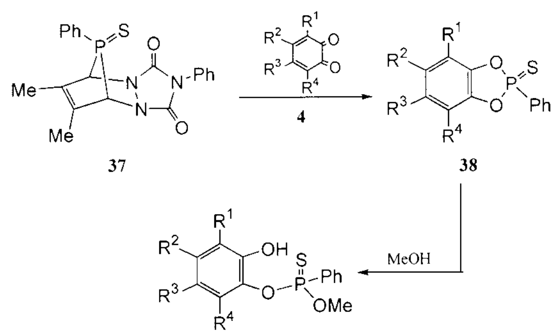
31 **32** **33**

The phosphonothioic dichlorides **34** (R = Ph, cyclo-C_6H_{11}) react with an equimolar amount of magnesium in the presence of benzil in tetrahydrofuran (THF) to give 1,3,2-dioxaphosphole 2-sulfides **36**, suggesting the intermediancy of phosphinothioylidenes **35**.[45]



34 **35** **36**

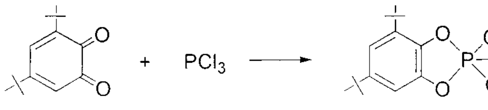
Phosphinothioylidene, generated by thermal cycloreversion from phosphine sulfide **37**, was trapped by [4 + 1]-cycloaddition with *o*-quinones **4** [$R^1R^2 = R^3R^4 = (CH)_4$; $R^1 = R^2 = R^3 = R^4 =$ Cl, Br; $R^1 = R^3 = t$-Bu, $R^2 = R^4 =$ H] to give dioxaphospholane sulfides **38**. Solvolysis of **38** with methanol affords the phosphonates **39**.[55]



37 **38** **39**

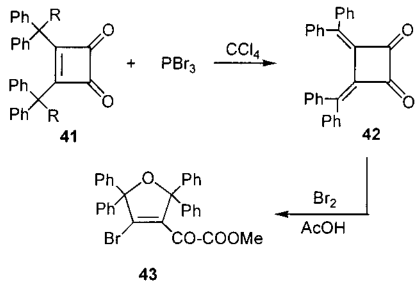
IV. Reactions with Halogenated Phosphorus Compounds

The nucleophilicity of the phosphorus lone pair of electrons decreases with increasing electronegativity of the substituents on trivalent phosphorus as PX_3 (X = F, Cl, Br). Phosphorus trichloride reacts with 3,5-di-*tert*-butyl-*o*-benzoquinone (1:1) in toluene at −60 °C to room temperature to give 96% yield of the cyclic adduct **40**,[56] whereas phosphorus tribromide

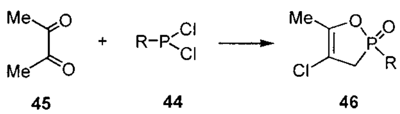


40

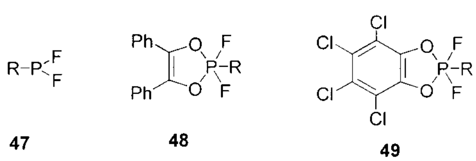
with cyclobutenedione derivatives **41** (R = R′ = OH; R = H, R′ = OH) in carbon tetrachloride at 0 °C affords 3,4-bis(diphenylmethylene)cyclobutane-1,2-dione **42**, which upon treatment with bromine in 99% acetic acid yields 2,2,5,5-tetraphenyl-3-bromo-4-methoxalyl-2,5-dihydrofuran (**43**)[57] in 45% yield.



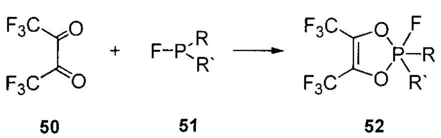
The reaction of phosphorus dichlorides **44** (R = Me, Et, Ph) with 2,3-butanedione (**45**) in benzene solution under carbon dioxide produces the cyclic enol esters of (2-chloro-3-oxobutyl)phosphonic acids **46**.[58,59]



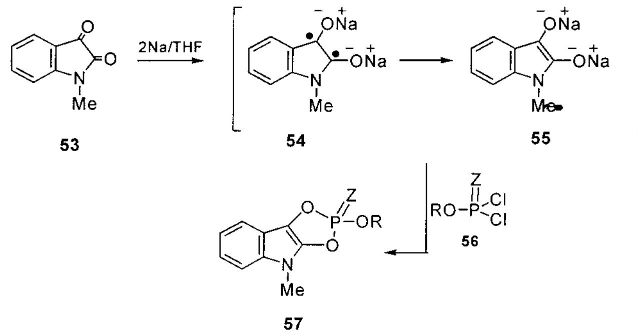
The oxidation of difluorophosphines **47** with benzil and *o*-chloranil leads to the corresponding difluorophosphoranes **48**[60] (R = Ph) and **49**[61] (R= *t*-Bu, CPh_3), respectively.



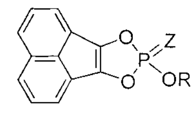
Hexafluorobiacetyl (**50**) reacts with phosphorus fluorides **51** [R = Ph, NEt_2, $N(CH_2 = CHCH_2)_2$, PrO, R′ = F; R = Ph, *p*-tolyl, R′ = NEt_2; RR′ = $O(CH_2)_2O$, *o*-$C_6H_4O_2$] in oxidative addition to form stable cyclic oxyphosphoranes **52**.[62]



Treatment of *N*-methylisatin (**53**) with sodium in dry tetrahydrofuran (THF) followed by addition of phosphorodichloridates **56** (Z = O; R = Et, Ph) and phosphorothiodichloridates **53** (Z = S, R = Et, Ph) gives the dioxaphospholes **57**.[63] The synthesis involves the initial formation of diradical dianion **54**, by electron transfer from sodium to diketones **53** by radical coupling to give the dianion **55**.[64]

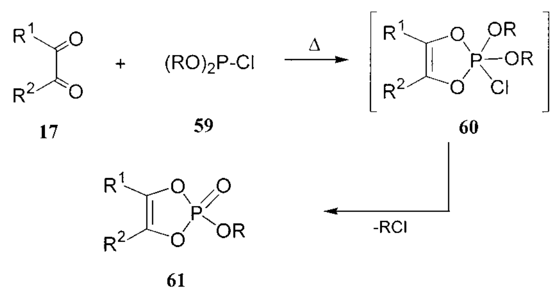


Similar reaction of acenaphthenequinone with **56** yields the corresponding dioxaphospholes **58**.[63]

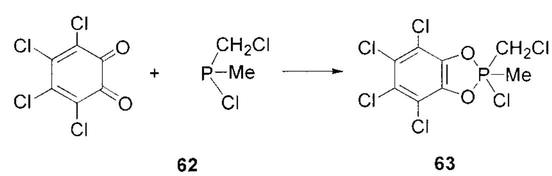


58

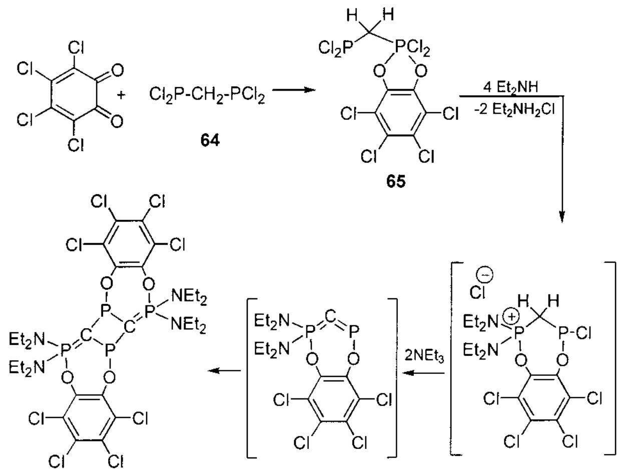
Dialkyl phosphorochloridites **59** (R = Et, Pr, Bu, *i*-Bu) with α-diketones **17** (R^1 = R^2 = Me, Ph) are heated in a sealed tube for 8−10 h at 100 °C (R^1 = R^2 = Me) and at 150 °C (R^1 = R^2 = Ph) to form 2-alkoxy-2-oxo-1,3,2-dioxaphospholes **61**, via intermediate **60**.[65]



o-Chloranil is added to the phosphorus atom of chloro(chloromethyl)methylphosphine (**62**) in benzene solution and reacted for 3 h to give the phosphorane **63**.[66]



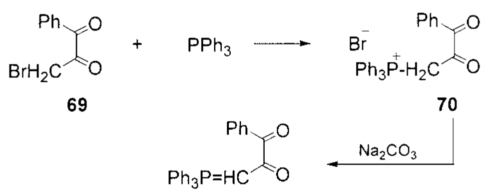
Partial oxidation of 1,1,3,3-tetrachloro-1,3-diphosphapropane (**64**) with tetrachloro-*o*-benzoquinone furnishes the methylene bridged λ^3P, λ^5P species **65**. Subsequent reaction with 4 equiv of diethylamine gives compound **66**, which has been identified by ^{31}P NMR and mass spectra. The addition of triethylamine to the cold solution of **66** in toluene, which is allowed to stand at room temperature for 23 days, produces the condensed ring system **68** with the P=C bonds connected to a central four-memberd ring through the intermediate **67**. Compound **68** displays crystallographic inversion symmetry, a short transannular P−P distance, and an extremely distorted tetrahedral coordination geometry at the four-membered ring phosphorus atom.[67]



64 65 66 67 68

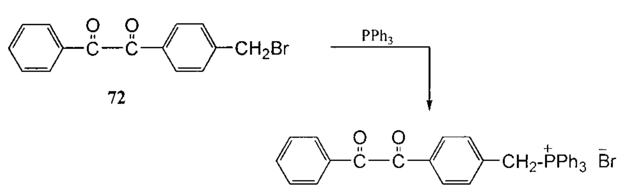
V. Reactions with Tertiary Phosphines

The reductive dehalogenation of a halogen in α-diketone by triphenylphosphine gives the stable C-phosphonium salt; for example, the reaction of triphenylphosphine with 3-bromo-1-phenyl-1,2-propanedione (**69**) in tetrahydrofuran (THF) yields the quaternary phosphonium salt **70**, which upon treatment with an aqueous solution of sodium carbonate produces [(benzoylcarbonyl)methylene]triphenylphosphorane (**71**).[68]



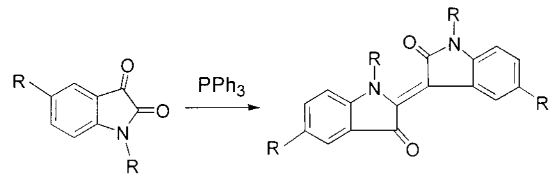
69 70 71

Similarly, 4-(bromomethyl)benzil (**72**) reacts with triphenylphosphine in benzene solution to give the phosphonium salt **73** in 89% yield.[69]



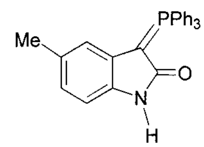
72 73

The reaction of triphenylphosphine with α-diketones is recommended as a convenient method for the preparation of dimeric ketones known to be widely used as dyestuffs.[70] So, isatin **74** (R = R′ = H) and *N*-methylisatin **74** (R = Me, R′ = H) react with triphenylphosphine in dry toluene for 20 h to give indirubin **75** in about 90% yield.[71]



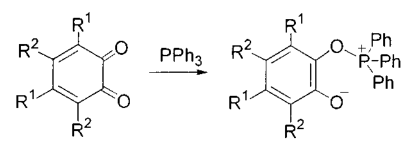
74 75

By the same manner, acenaphthenequinone, naphtho[2,1-*b*]furan-1,2-dione, and benzo[*b*]thiophene-2,3-dione react with triphenylphosphine to give the corresponding dimeric structures.[71,72] While 5-methylisatin **74** (R = H, R′ = Me) reacting with triphenylphosphine in a 1:2 molar ratio in boiling toluene for 6 h forms the ylidenetriphenylphosphorane **76**.[73]



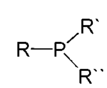
76

Horner and co-workers[74,75] reported that the reaction of triphenylphosphine with *o*-benzoquinone **77** ($R^1 = R^2 =$ H) and its tetrachloro derivative **77** ($R^1 = R^2 =$ Cl) gives the phosphonium enolate **78**, which also obtained from the photochemical reaction of phenanthrenequinone **77** [$R^1R^2 = (CH)_4$] with triphenylphosphine in the presence of water.[76]



77 78

On the other hand, the reaction of tertiary phophines **79** with phenanthrenequinone is reported by Ramirez et al.[77] They found that trimethylphosphine **79** (R = R′ = R″ = Me) in benzene solution at 25 °C yields the unstable adduct, suggesting that the oxyphosphorane **80** [$R^1R^2 = (CH)_4$, R = R′ = R″ = Me] and the open dipolar ion **81** exist in rapid equilibrium.[77]



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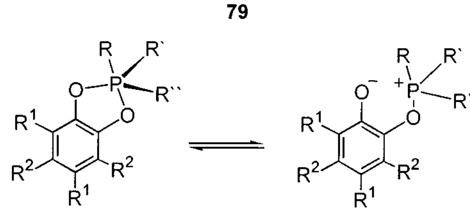
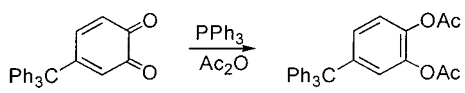


80 81

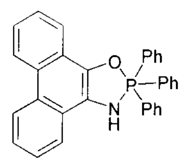
For the given *o*-quinones **77** [$R^1R^2 = (CH)_4$; $R^1 =$ *t*-Bu, $R^2 =$ H], the presence of phenyl rings instead of alkyl groups on the phosphorus in **79** favors the oxyphosphorane structures **80**.[77,78]

4-Triphenylmethyl-1,2-benzoquinone (**82**) reacts with triphenylphosphine in acetic anhydride at room temperature to give 3,4-diacetyloxytetraphenylmethane **83**.[79]



82 **83**

The reaction of phenanthrenequinone **77** [R^1R^2 = $(CH)_4$] and 3,5-di-*tert*-butyl-*o*-benzoquinone **77** (R^1 = *t*-Bu, R^2 = H) with triphenylphosphine in pyridine at 80−90 °C and in the presence of liquid ammonia gives the phosphole derivative **84**, which has a cyclic structure in solution and in solid state, while the adduct **85** shows a tautomeric equilibrium with the iminophosphorane **86** in solution.[80]



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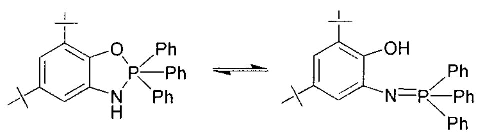
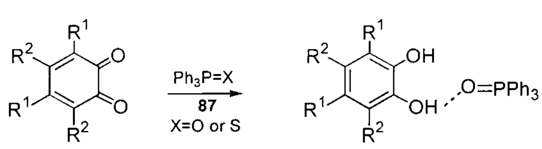


85 **86**

VI. Reactions with Phosphine Oxides and Phosphine Sulfides

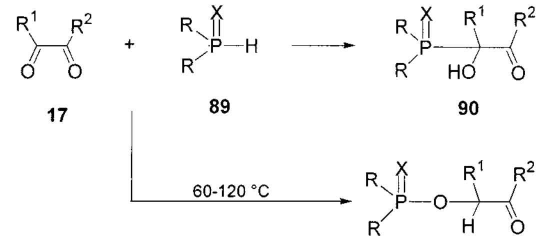
In the phosphine oxides the d-orbital system is presumably fixed in the most energetically favorable orientation with respect to the P−O bond, to allow two 3d orbitals to overlap with the lone pairs on oxygen. The phosphoryl oxygen atom (P=O) shows little of the nucleophilicity of the P=C or P=N groups, but under vigorous conditions, reactions do occur.[81] Triphenylphosphine oxide (**87**, X = O) is added to 3,5-di-*tert*-butyl-1,2-benzoquinone **77** (R^1 = *t*-Bu, R^2 = H) in boiling methanol and water (1:1) and reacted for 18 h to yield the hydrogen-bonded complex **88** (R^1 = *t*-Bu, R^2 = H).[78]



77 **88**

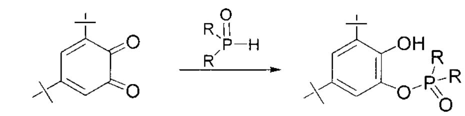
The hydrogen-bonded complex **88** (R^1 = R^2 = Cl) is also obtained with elemental sulfur when an equimolar mixture of triphenylphosphine sulfide (**87**, X = S) and *o*-chloranil **77** (R^1 = R^2 = Cl) was heated under reflux in benzene solution. The proposed mechanism has been explained.[82]

The reaction of dibutylphosphine sulfide (**89,** R = Bu, X = S) with α-diketones **17** (R^1 = R^2 = Me, Ph) at about 35 °C affords the α-hydroxy derivatives **90**. When the additions take place in the presence of sodium ethoxide at 60−120 °C for about 4 h, the products of addition isomerize to **91**.[83]



17 **89** **90** **91**

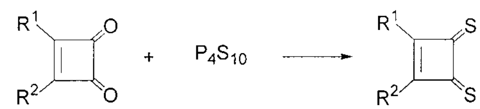
3,5-Di-*tert*-butyl-*o*-benzoquinone reacts with dimethyl- and diphenylphosphine oxides (**89,** R = Me, Ph; X = O) to furnish the catechol phosphinic acid esters **92**.[84]



92

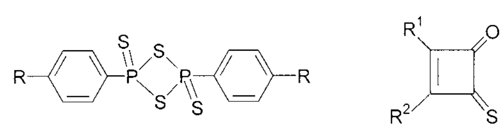
VII. Reactions with Phosphorus Pentasulfide and Lawesson's Reagent

Phosphorus pentasulfide is the sulfur-transfer reagent, though it may lead to bis-thionation. When squaric acid derivative **93** (R^1 = R^2 = NHBu) in dichloromethane was treated with phosphorus pentasulfide, it gave the dithio analogue **94** in about 70% yield.[85]



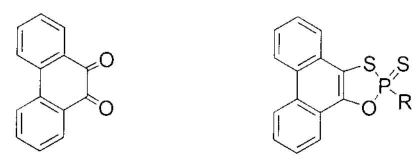
93 **94**

The highly regioselective monothionation of squaric acid derivatives **93** [R^1 = O-*i*-Pr, R^2 = Ph; R^1 = O-*i*-Pr, R^2 = Bu; R^1 = O-*i*-Pr, R^2 = 4-$MeOC_6H_4$; R^1 = O-*i*-Pr, R^2 = 4-$Me_2NC_6H_4$; R^1 = NEt_2, R^2 = Ph; R^1 = NBz_2, R^2 = OEt; R^1 = $N(CH_2)_2O$, R^2 = OEt] with 0.5 mol equiv of Lawesson's reagent **95** (R = OMe) in dichloromethane at room temperature affords 4-thioxocyclobut-2-enones **96**.[86] An X-ray structural investigation of single crystal of **96** (R^1 = O-*i*-Pr, R^2 = Ph) was carried out.[86]



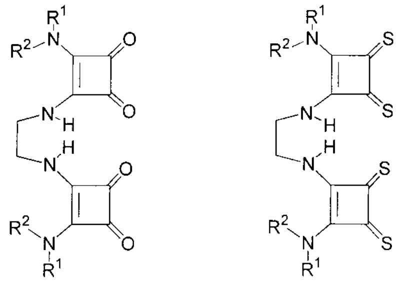
95 **96**

Phenanthrooxathiaphosphole 2-sulfide derivatives **97** (R = OMe, OPh) are formed from the reaction of 9,10-phenanthrenequinone with Lawesson's reagent **95** (R = OMe, OPh) in boiling toluene for 2 h.[87]



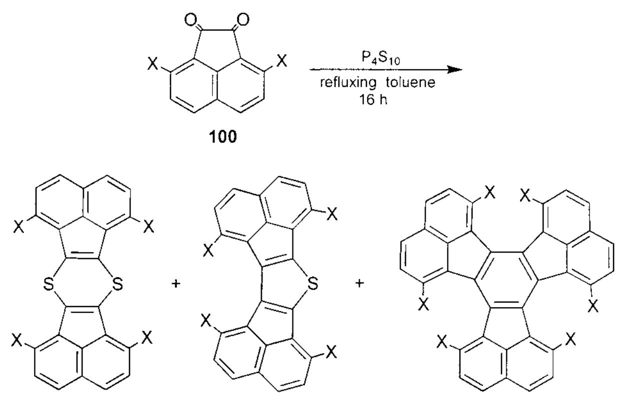
97

Reaction of bis(squaramides) **98** (R^1 = Bu, R^2 = H; R^1 = R^2 = Et, Bu) with excess phosphorus pentasulfide gives the analogous tetrathio derivatives **99**.[88]



98 **99**

Acenaphthenequinone **100** (X = H, Br) with an 8-fold molar excess of phosphorus pentasulfide in boiling toluene for 16 h gives the diacenaphtho[1,2-*b*:1′,2′-*e*][1,4]dithiin **101** (X = H, Br), diacenaphtho-[1,2-*b*:1′,2′-*d*]thiophene **102** (X = H, Br), and decacyclene **103** (X = H).[89]

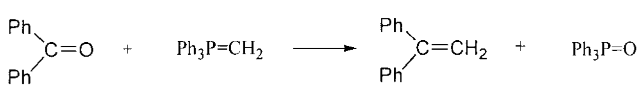


100

101 **102** **103**

VIII. Reactions with Wittig Reagents

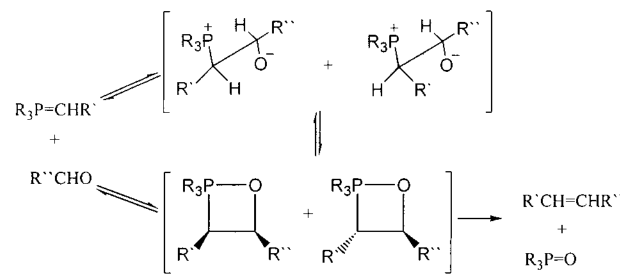
In 1953, Wittig and Geissler[8] found that the reaction of benzophenone (**104**) with methylene-(triphenyl)phosphorane (**105**) gives 1,2-diphenylethylene (**106**) and triphenyl phosphine oxide in almost quantitative yield.



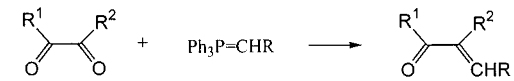
104 **105** **106**

The mechanism of the Wittig reaction is commonly expressed in terms of two steps: (i) nucleophilic addition of phosphorus ylide to the carbonyl compound to give a betaine species and (ii) irreversible decomposition of the betaine to form alkene and phosphine oxide.[90−99]

The Wittig reaction of α-dicarbonyl compounds **17** (R^1 = R^2 = H, Me, Ph, 2-furyl) with methylene-(triphenyl)phosphoranes **107** (R = Et, Ph, CN, COMe, COPh, COOMe, COOEt) affords the alkene formation

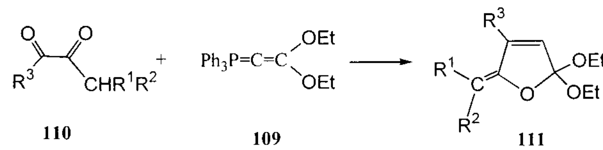


at only one of the two possible carbonyl groups[100−106] to produce (*Z*)- and (*E*)-isomeric adducts **108**.[102,106]



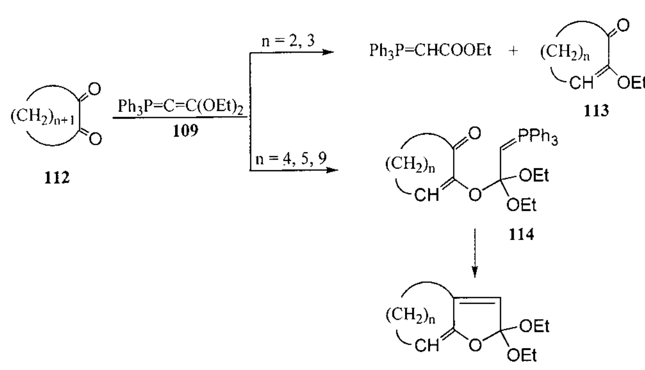
17 **107** **108**

The reaction of 2,2-diethoxyvinylidene(triphenyl)-phosphorane (**109**) with enolizing 1,2-diketones **110** (R^1 = H, R^2 = R^3 = Ph; R^1 = R^2 = Me, R^3 = Ph) gives the furan derivatives **111**.[107]



110 **109** **111**

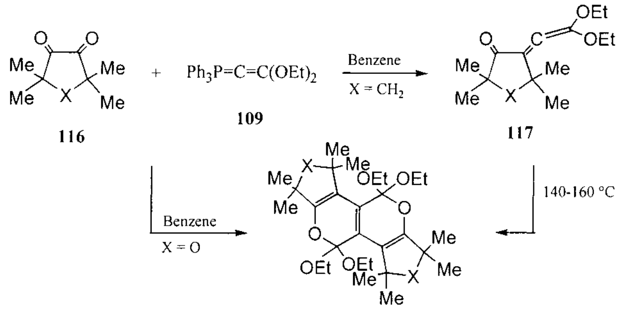
Furthermore, the phosphorane **109** reacts with enolizing cyclic 1,2-diketones **112** (*n* = 2, 3) to yield ethoxycarbonylmethylene(triphenyl)phosphorane and the cyclic adducts **113**, whereas diones **112** (*n* = 4, 5, 9) affords the corresponding phosphoranes **114**. An intramolecular Wittig reaction for compounds **114** spontaneously gives the furan derivatives **115**.[108]



112 **113** **114** **115**

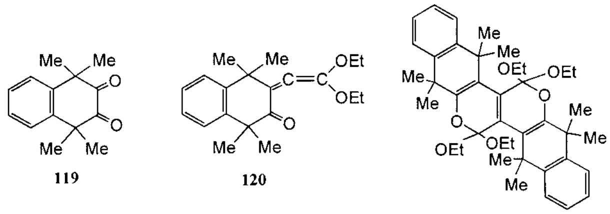
3,3,5,5-Tetramethyltetrahydro-1,2-cyclopentanedione (**116**, X = CH_2) with phosphonium ylide **109** in benzene solution yields the allene product **117**, which upon heating at 140−160 °C forms the dimeric structure **118** (X = CH_2).[109,110] On the other hand, 3,4-furandione derivative **116** (X = O) affords directly the dimeric adduct **118** (X = O).[110]

Similarly, treatment of 1,1,4,4-tetramethyltetralin-2,3-dione (**119**) with the same ylide **109** gives the



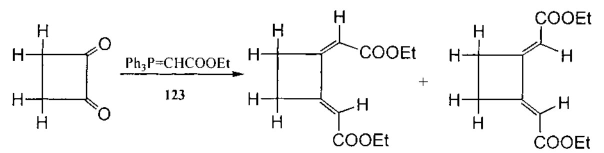
116 109 117 118

allene structure **120**, which on prolonged heating at 100 °C forms about 1% yield of the dimer **121**.[111]



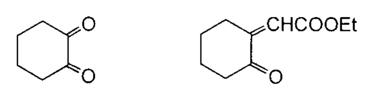
119 120 121

Cyclobutane-1,2-dione (**122**) undergoes bis-Wittig reaction with ethoxycarbonylmethylene(triphenyl)-phosphorane (**123**) to produce (*Z,E*)- and (*E,E*)-dimethylenecyclobutane (**124a**, 28% yield; **124b**, 10% yield), respectively.[100]



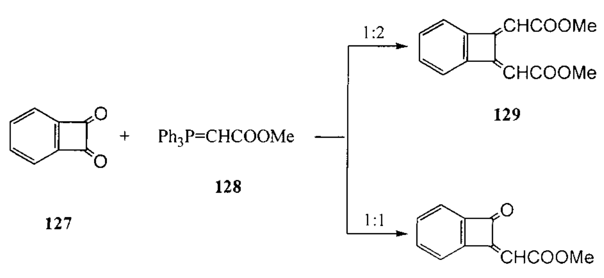
122 124a 124b

The reaction of cyclohexane-1,2-dione (**125**) with the same phosphonium ylide **123** affords the α,β-unsaturated ketone **126**.[100]



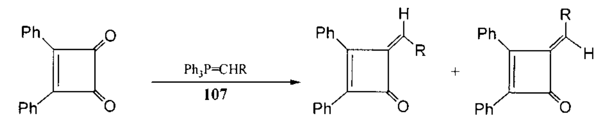
125 126

The reaction of benzocyclobutenedione (**127**) with 2 mol equiv of methoxycarbonylmethylene(triphenyl)-phosphorane (**128**) in dichloromethane at room temperature affords 1,2-dimethylenebenzocyclobutene **129** in 85% yield.[112] Carrying out the same reaction using 1 mol equiv of ylide forms methylenebenzocyclobutanone **130** in 93% yield.[112]



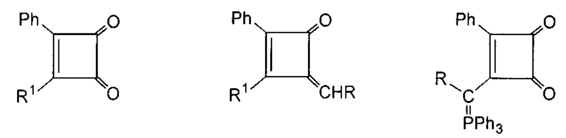
127 128 129 130

Diphenylcyclobutenedione (**131**) reacts with methylene(triphenyl)phosphoranes **107** (R = COOMe, COOEt, $COOCMe_3$, $COOCH_2Ph$, COPh) in boiling benzene to give (*Z*)- and (*E*)-isomers of cyclobutenones **132**. Also, treatment of dione **131** with ylide **107** (R = aryl) leads to the formation of only (*Z*)-isomer.[113]



131 (*Z*)-132 (*E*)-132

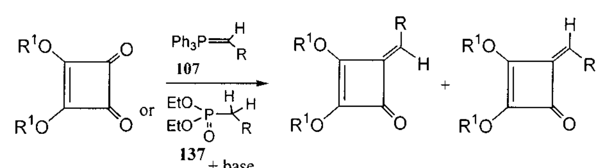
The reaction of phenylcyclobutenedione derivatives **133** (R^1 = OMe, SMe) with phosphonium ylides **107** (R = Ph, substituted Ph, 1-naphthyl) in tetrahydrofuran or dimethylformamide gives the corresponding cyclobutenones **134**, while 3-phenoxy-4-phenyl-3-cyclobutene-1,2-dione (**133**, R^1 = OPh) with ylides **107** (R = COOEt, COPh) affords (*Z*)-isomers of **134** beside the phosphoranes **135**, resulting from substitution of phenoxy group.[114]



133 134 135

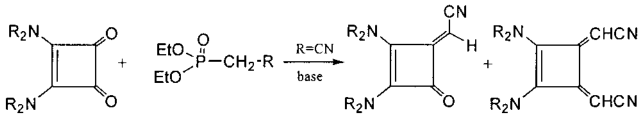
3-Bromo-4-phenyl-3-cyclobutene-1,2-dione (**133**, R^1 = Br) reacts with the ylides **107** to produce the corresponding cyclobutenones **134** (R = Ph, *o*-, *m*-tolyl, *o*-ClC_6H_4), by a Wittig reaction, and **135** (R = COOMe, COOEt, $COOCH_2Ph$, $COOCMe_3$, Bz, Ph, *o*-, *m*-tolyl, *o*-ClC_6H_4), by transylidation.[115]

The olefination of dialkyl squarates **136** (R^1 = allyl, Bn, i-Pr, 3-pentyl, 2-methyl-4-pentyl) by Wittig reaction using Wittig ylides **107** (R = COOMe, COOEt, $COOCMe_3$, CN) in tetrahydrofuran or benzene gives the corresponding alkylidene products **138** as a mixture of two isomers (*E* and *Z*) in ratio 2:1.



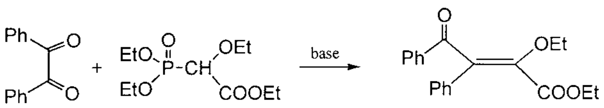
136 (*E*)-138 (*Z*)-138

Similarly, Horner–Emmons olefination of squarates **136** by phosphonates **137** in tetrahydrofuran in the presence of sodium hydride as a base affords only (*Z*)-isomer **138**.[116] The Wittig–Horner reaction of diethyl (cyanomethylene)phosphorane (**137**, R = CN) with squaric acid diamides **139** (NR_2 = NMe_2, pyrrolidino, piperidino) in the presence of a base yields the monoalkene derivative **140** (NR_2 = pyrrolidino) as (*E*)-isomer and 2:1 adducts **141** (NR_2 = NMe_2, piperidino) as (*Z,E*)- and (*Z,Z*)-isomers.[117]



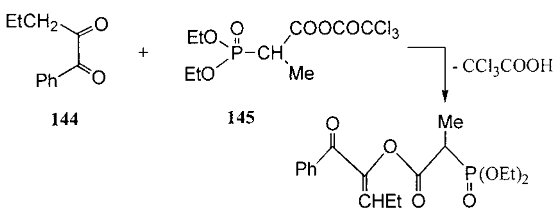
139 **137** (*E*)-**140** **141**

Reaction of benzil with Wittig−Horner reagent **142** in toluene in the presence of a base forms ethyl *β*-benzoyl-α-ethoxycinnamate (**143**) in 70% yield.[118]



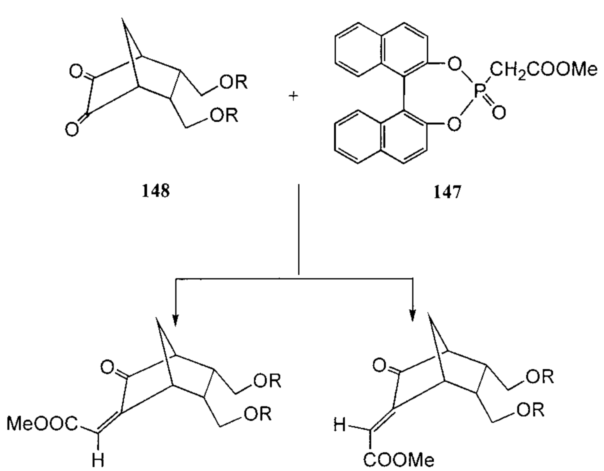
142 **143**

The Wittig−Horner reaction of 1-phenylpentane-1,2-dione (**144**) with phosphorus reagent **145** in tetrahydrofuran in the presence of triethylamine gives the phosphonate **146** in 47% yield.[119]



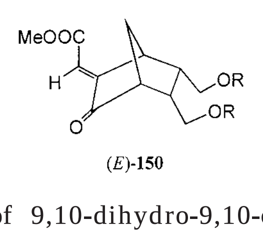
146

The reaction of a chiral phosphonate reagent (*S*)-**147** with *meso*-α-diketone **148** (R = $SiPh_2t$-Bu) in tetrahydrofuran at −78 °C yields nonracemic (*Z*)-**149** as a major isomer and (*E*)-**149** in trace amounts.[120]



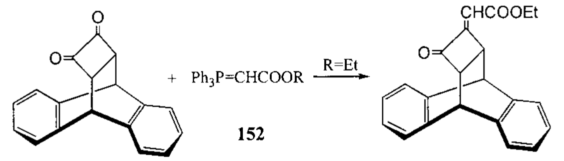
(*Z*)-**149** (*E*)-**149**

When the above reaction is carried out between the phosphonate **147** and α-diketones **148** (R = Ac, Bn), the corresponding (*Z*)-**149** and (*E*)-**150** are formed in 75% and 25% yield, respectively.[121]



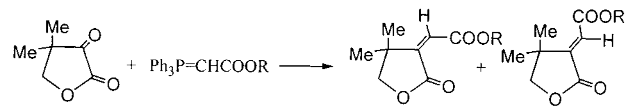
(*E*)-**150**

Treatment of 9,10-dihydro-9,10-cyclobutanoanthracene-13,14-dione (**151**) with ethoxycarbonylmethylene(triphenyl)phosphorane (**152**, R = Et) yields **153** as a mixture of two isomers.[122]

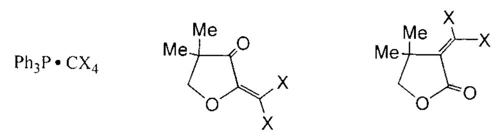


151 **153**

4,4-Dimethyloxolan-2,3-dione (**154**) reacts with alkoxycarbonylmethylene(triphenyl)phosphoranes (**152**, R = Me, Et) in tetrahydrofuran at room temperature to produce a mixture of (*Z*)- and (*E*)-isomers of alkyl (dihydro-4,4-dimethyl-2-oxo-3(2*H*)-furanylidene)acetates (**155**).[123,124] While triphenylphosphine carbon tetrahalide reagents **156** (X = Cl, Br) with the same dione **154** form the respective dihalomethyleneoxolanes **157** and **158**.[125]

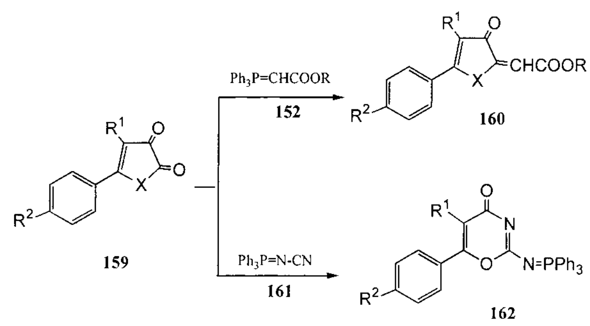


154 **152** (*Z*)-**155** (*E*)-**155**



156 **157** **158**

The reaction of alkoxycarbonylmethylene(triphenyl)phosphoranes (**152**, R = Me, Et) with α-diketones **159** (R^1 = Cl, Br, Ph; R^2 = H, Me, OMe, OEt, Br; X = O, NH) affords the corresponding (*Z*)-isomers of 2-alkylidene derivatives **160**.[126−128] The structure

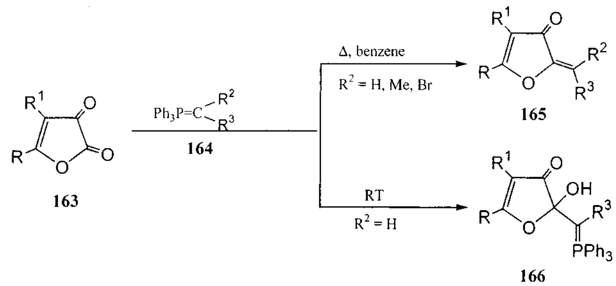


159

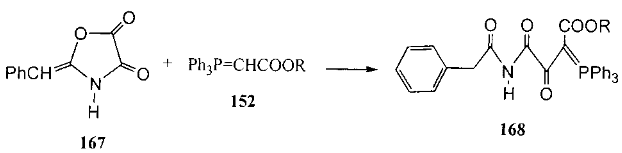
of compound **160** (R^1 = Ph, R^2 = H, X = NH) was identified by X-ray analysis.[128] On the other hand, imino(triphenyl)phosphorane (**161**) with aryldihydrofurandiones **159** (R^1 = H; R^2 = H, Me; X = O) gives 6-aryl-2-[(triphenylphosphoranylidene)amino]-1,3-oxazin-4-ones (**162**), via a thermolysis/[4 + 2]-cycloaddition, sequence involving intermediate aroylketenes.[129]

The Wittig reaction of 5-aryl-2,3-furandiones **163** (R = aryl; R^1 = H, Br, COPh) with the phosphoranes **164** (R^2 = H, Me, Br; R^3 = COOMe, COMe, COC_6H_4-Br-4, COC_6H_4Cl-4) in boiling benzene forms the 2-alkylidene derivatives **165**.[130] The structure of **165** (R = Ph, R^1 = R^2 = H, R^3 = COOMe) was identified by X-ray analysis.[130]

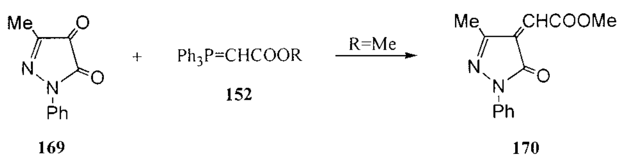
When the same reaction is carried out at room temperature, the phosphoranylidene derivatives **166** are formed in good yields.[130−132]



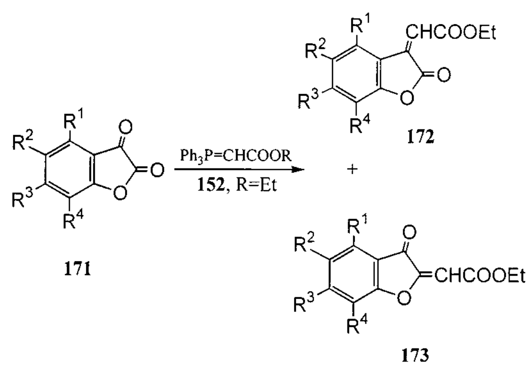
2-Benzylidene-4,5-dione (**167**) reacts with stabilized ylides **152** (R = Me, Et) in boiling benzene to give 1:1 adducts formulated as **168**.[133]



When 3-methyl-1-phenyl-2-pyrazolin-4,5-dione (**169**) reacts with methoxycarbonylmethylene(triphenyl)-phosphorane (**152**, R = Me), the alkylidene **170** is formed as a mixture of (*Z*)- and (*E*)-isomers.[134]

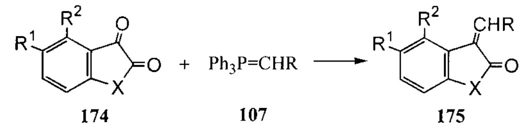


The Wittig reaction of benzofuran-2,3-dione (**171**, $R^1 = R^2 = R^3 = R^4$ = H) with ethoxycarbonylmethylene(triphenyl)phosphorane (**152**, R = Et) gives a mixture of 3-alkylidene-2(3*H*)-benzofuranone **172** and 2-alkylidene-3(2*H*)-benzofuranone **173**,[135] whereas

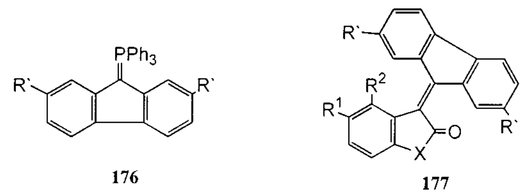


the electron-donating substituent on the aromatic ring in **171** ($R^1 = R^3$ = OMe, R^2 = H, R^4 = Cl) with the same ylide affords only 2-alkylidene-3(2*H*)-(7-chloro-4,6-dimethoxy)benzofuranone (**173**), with high regioselectivity.[135] Treatment of 7-*tert*-butyl-5-methoxy-2,3-dihydrofuran-2,3-dione (**171**, $R^1 = R^3$ = H, R^2 = OMe, R^4 = *t*-Bu) with ylide **152** (R = Et) in benzene solution at room temperature yields compound **172** as a mixture of (*Z*)- and (*E*)-isomers.[136,137]

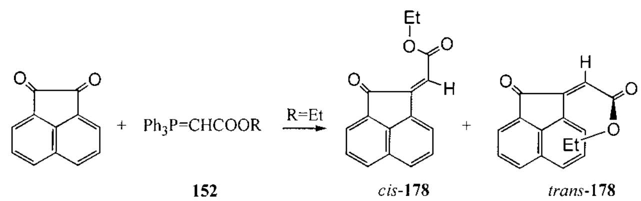
The reaction of isatins **174** (X = NH, NAc; R^1 = H, Me; R^2 = H), benzo[*b*]thiophene-2,3-diones **174** (X = S; R^1 = H, Me; R^2 = H), and naphtho[2,1-*b*]furan-1,2-dione **174** [X = O, $R^1R^2 = (CH)_4$] with phosphonium ylides **107** (R = Ph, COMe, COPh, COOMe, COOEt, CN) leads to the formation of 3-alkylidene derivatives **175**.[73,103,104,138−145]



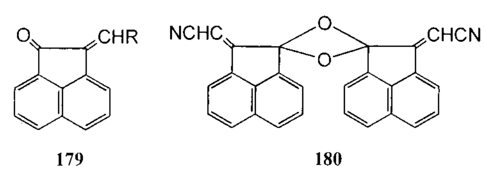
Fluorenylidene(triphenyl)phosphorane (**176**, R′ = H) reacts with α-diketones **174** [X = O, $R^1 = R^2$ = H; X = S, $R^1 = R^2$ = H; X = O, R^1 R^2 = $(CH)_4$] to give the fluorene-9-ylidene derivatives **177**.[72]



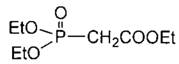
Reaction of acenaphthenequinone with several Wittig reagents has been studied.[104,146−149] Ethoxycarbonylmethylene(triphenyl)phosphorane (**152**, R = Et) reacts with acenaphthenequinone in ethanol at room temperature to form cis- and trans-isomers of ethoxycarbonylmethyleneacenaphthenone **178**.[146] Lefkaditis et al.[147,148] reported that the only product *cis*-**178** is obtained.



Treatment of acenaphthenequinone with phosphonium ylides **107** (R = H, Me, aryl, COMe, COPh, COC_6H_4Cl-4), gives the corresponding acenaphthenones **179** in fairly good yields,[146] whereas using cyanomethylene(triphenyl)phosphorane (**107**, R = CN) gives cyanomethyleneacenaphthenone (**179**, R = CN) and the dimeric structure **180**.[149]



The reaction of acenaphthenequinone with triethylphosphonoacetate (**181**) in ethanol in the presence of sodium ethoxide gives the two dimeric products having structures **182** and **183**, respectively.[150]



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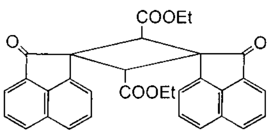

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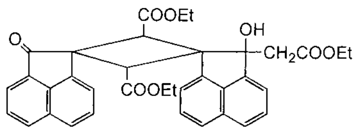
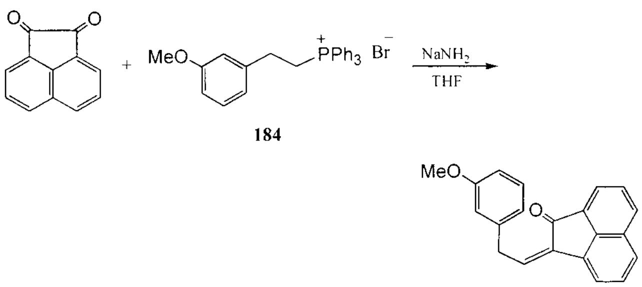


183

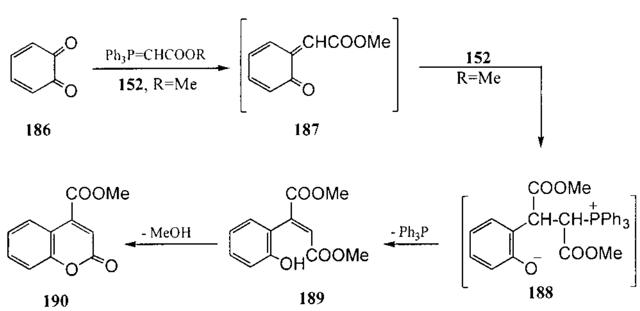
Wittig reaction of *m*-methoxyphenethyl(triphenyl)-phosphonium bromide (**184**) with acenaphthene-quinone in boiling tetrahydrofuran under nitrogen atmosphere and in the presence of sodium amide yields 1-[2-(*m*-anisyl)ethylidene]acenaphthenone (**185**).[151]



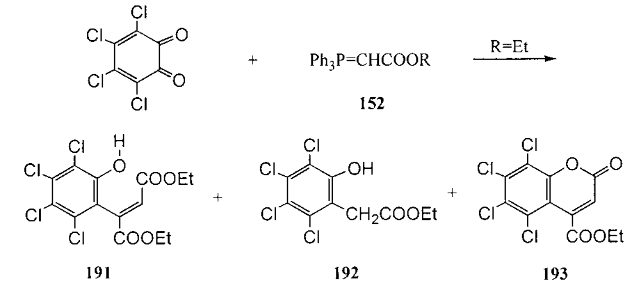
184

185

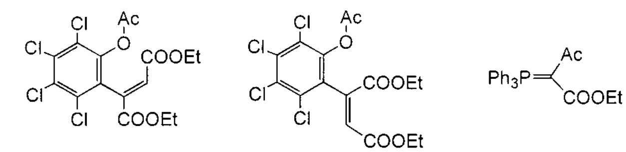
o-Benzoquinone **186** reacts with methoxycarbonyl-methylene(triphenyl)phosphorane (**152**, R = Me) to form the monoalkene **187**, followed by Michael's addition of a second phosphorane molecule to give the intermediate **188**. The resulting phosphonium betaine **188** eliminates triphenylphosphine to produce (*o*-hydroxyphenyl)fumaric acid esters **189**, which cyclizes via ejection of methanol to afford coumarin-4-carboxylic acid methyl ester (**190**).[152]



Tetrachloro-1,2-benzoquinone reacts with ethoxy-carbonylmethylene(triphenyl)phosphorane (**152**, R = Et) in dichloromethane solution to form diethyl (2,3,4,5-tetrachloro-6-hydroxyphenyl)fumarate (**191**) as the major product, along with unexpected product ethyl (2,3,4,5-tetrachloro-6-hydroxyphenyl)acetate (**192**) and the coumarin derivative **193**.[153]

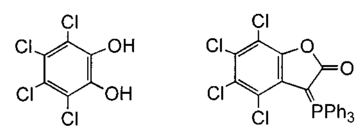


Repetition of the above reaction in acetic anhydride at 60 °C yields diethyl (2-acetoxy-3,4,5,6-tetrachloro-phenyl)fumarate (**194**), its maleate derivative **195**, and acetylated ylide **196**.[154]



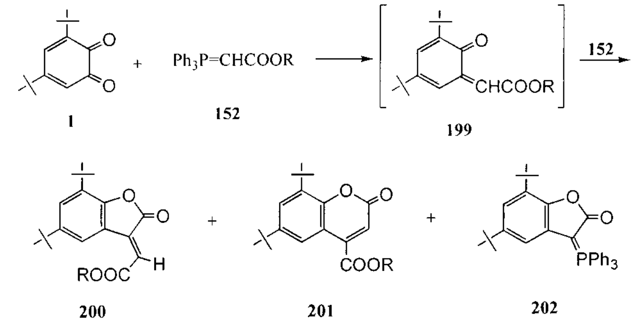
194 195 196

When the *o*-chloranil is added portionwise to a stirred solution of ylide **152** (R = Et) in the presence of triphenylphosphine in dichloromethane, a mixture of tetrachlorocatechol (**197**) in 13% yield, ethyl (2,3,4,5-tetrachloro-6-hydroxyphenyl)acetate (**192**) in 37% yield, and 4,5,6,7-tetrachloro-3-triphenylphosphora-nylidenebenzo[*b*]furan-2(3*H*)-one (**198**) in a small amount are obtained.[154]



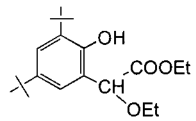
197 198

The reaction of 3,5-di-*tert*-butyl-1,2-benzoquinone (**1**) with ethoxycarbonylmethylene(triphenyl)phos-phorane (**152**, R = Et) and/or its methyl analogue (**152**, R = Me) in boiling dichloromethane forms a mixture of (*E*)-ethyl (5,7-di-*tert*-butyl-2,3-dihydro-2-oxobenzo[*b*]furan-3-ylidene)acetate (**200**), the coumarin derivative **201**, and 5,7-di-*tert*-butyl-3-triphen-ylphosphoranylidenebenzo[*b*]furan-2(3*H*)-one (**202**).[153] Repetition of the above reaction at room temperature for 3 h gives the same products.



Reaction of the *o*-quinone **1** with 1 mol equiv of ethoxycarbonylmethylene(triphenyl)phosphorane (**152,** R = Et) in boiling ethanol gives ethyl (3,5-di-*tert*-

butyl-2-hydroxyphenyl)ethoxyacetate (**203**), along with compounds **200**, **201**, and **202**.[153]



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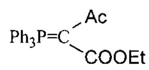
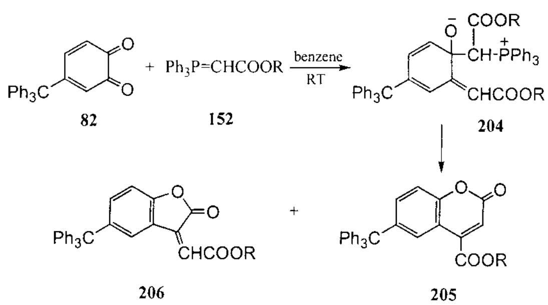


196

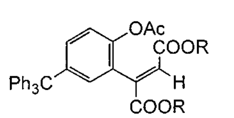
The same quinone **1** reacts with 2 mol equiv of ylide **152** (R = Et) in acetic anhydride at 60 °C to form a mixture of compounds **200**, **201**, and **196**.[154]

In 1991, Abdou et al.[155] found that the reaction of 3,5-di-*tert*-butyl-*o*-benzoquinone (**1**) with phosphonium ylides **152** (1 or 2 mol equiv) in benzene at room temperature affords the monosubstituted α,*β*-unsaturated esters **199**, whereas the same reaction in boiling benzene using 2 mol equiv of ylide **152** gives only the coumarin derivatives **201** in good yields.

4-Triphenylmethyl-1,2-benzoquinone (**82**) with alkoxycarbonylmethylene(triphenyl)phosphoranes (**152**) in benzene at room temperature gives the adduct **204**, which upon heating in toluene yields 4-alkoxycarbonyl-6-triphenylmethyl-2*H*-1-benzopyran-2-ones (**205**) and 5-triphenylmethyl-3-alkoxycarbonylmethylenebenzo[*b*]furan-2(3*H*)-ones (**206**) as a mixture of (*E*)- and (*Z*)-isomers.[156]



When the above reaction takes place in acetic anhydride at room temperature, the fumarates **207**, maleates **208**, benzofuran derivatives **209** (R^1 = H, R^2 = CPh_3; R^1 = CPh_3, R^2 = H), and diacetoxy compound **210** are formed.[79]



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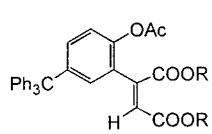

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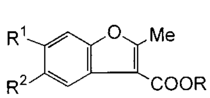

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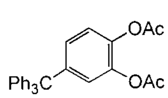
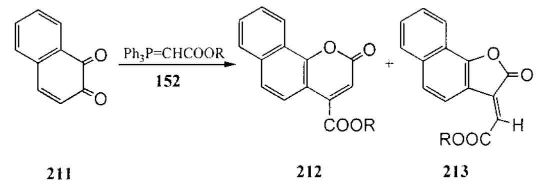
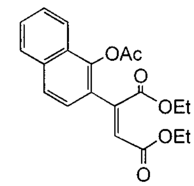


210

Reaction of *o*-naphthoquinone (**211**) with ethoxycarbonylmethylene(triphenyl)phosphorane (**152**, R = Et) and/or its methyl analogue (**152**, R = Me) gives, beside the coumarin derivatives **212** previously reported,[152] the *γ*-lactones **213**.[153]

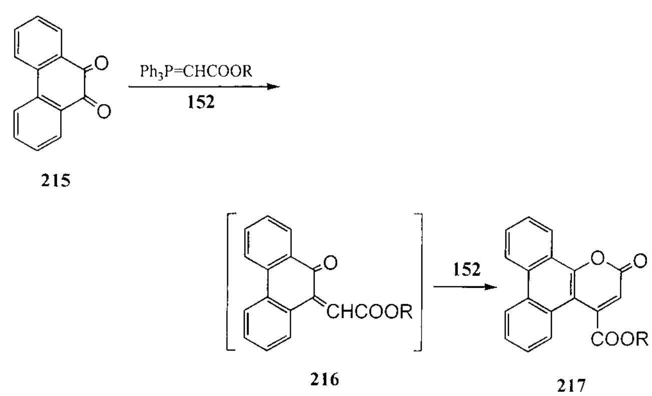


When acetic anhydride is used as a solvent in the above reaction, diethyl (1-acetoxy-2-naphthyl)maleate (**214**) and the coumarin derivative **212** are obtained.[154]

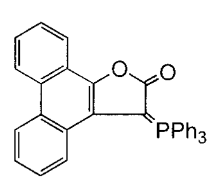


214

The reaction between phenanthrene-9,10-quinone (**215**) and phosphonium ylides **152** was first reported by Shechter and co-workers.[157] They found that the *o*-quinone **215** reacts with equimolar amounts of ylide **152** (R = Et) to give ethyl (9,10-dihydro-10-oxo-9-phenanthrylidene)acetate (**216**, R = Et). Soon afterward, Bestmann and Lang reported[152] that the reaction between the same quinone **215** and 2 mol equiv of ylides **152** affords the coumarin derivatives **217**. Also, the same result was obtained by Nicolaides et al.[153]

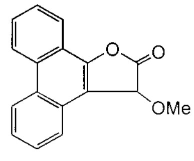


Treatment of *o*-quinone **215** with phosphonium ylide **152** (R = Et) in boiling dichloromethane in the presence of triphenylphosphine produces 3-(triphenylphosphoranylidene)phenanthro[9,10-*b*]furan-2(3*H*)-one (**218**) in 79% yield.[154]



218

The reaction of phenanthrenequinone (**215**) with the ylide **152** (R = Et) was studied in boiling methanol and in acetic anhydride at 60 °C. In the case of boiling methanol, it gives 3-methoxyphenanthro[9,10-*b*]furan-2(3*H*)-one (**219**, 48%) and the coumarin **217** (35%). While, in acetic anhydride, a mixture of diethyl (10-acetoxy-9-phenanthryl)fumarate (**220**, 62%), coumarin **217** (25%), and the unexpected ethyl 2-methylphenanthro[9,10-*b*]furan-3-carboxylate (**221**, 7%) is formed.[154]



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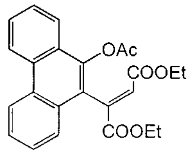

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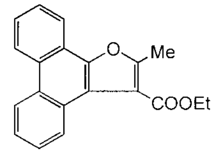
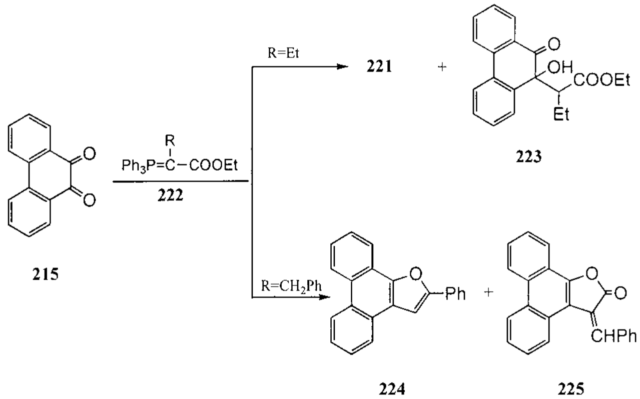
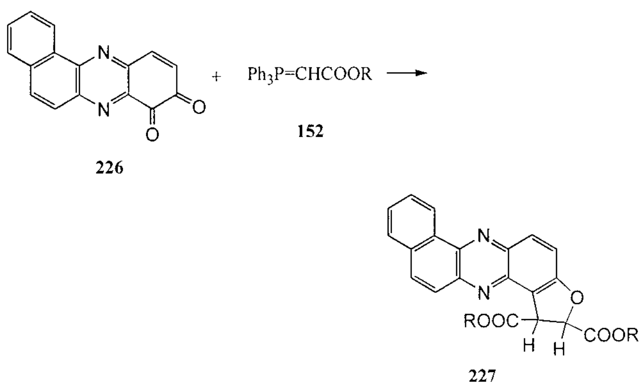


221

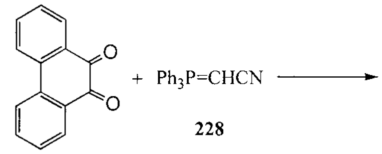
α-Ethylethoxycarbonylmethylene(triphenyl)phosphorane (**222**, R = Et) reacts with *o*-quinone **215** to form furan derivative **221** with compound **223**.[158] On the other hand, the reaction of ylide **222** (R = CH_2-Ph) with the same quinone affords phenanthro[9,10-*b*]furan derivatives **224** and **225**, respectively.[158]



Benzo[*a*]phenazine-8,9-dione (**226**) undergoes Wittig reaction with alkoxycarbonylmethylene(triphenyl)-phosphoranes (**152**) in tetrahydrofuran solution at room temperature to produce benzo[*a*]furo[3,2-*h*]-phenazine-1,2-dicarboxylates (**227**).[138]



Wittig reaction of cyanomethylene(triphenyl)phosphorane (**228**) with phenanthrenequinone (**215**) in boiling benzene for 6 h produces a mixture of 2,3-dicyanophenanthro[9,10-*b*]furan (**229**), 2-(9-hydroxyphenanthren-10-yl)-1,2-dicyanoethylene (**230**), and phosphonium ylide **231**.[149]



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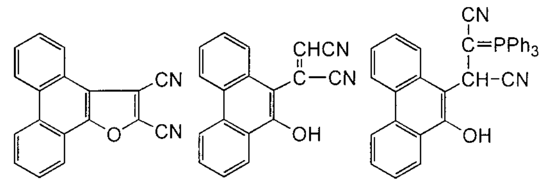
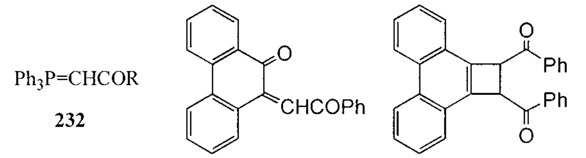


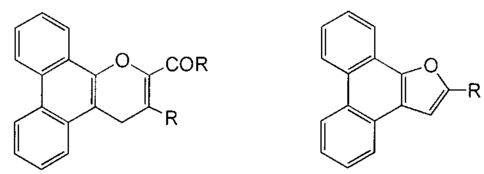
229 **230** **231**

Treatment of phenanthrenequinone (**215**) with benzoylmethylene(triphenyl)phosphorane (**232**, R = Ph) affords the mono-olefination adduct **233**, while using another molecule of same ylide **232** gives fused cyclobutene **234**.[157]

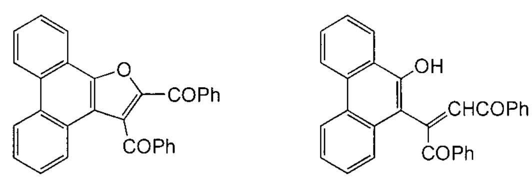


233 **234**

In 1989, Nicolaides et al.[159] reported that the reaction of benzoylmethylene(triphenyl) phosphorane (**232,** R = Ph) with phenanthrenequinone (**215**) in dichloromethane solution forms a mixture of the corresponding products **235** (R = Ph), **236** (R = Ph), **237**, and **238**, while using acetylmethylene(triphenyl)-phosphorane (**232**, R = Me) with the same quinone **215** leads to the formation of compounds **235** (R = Me) and **236** (R = Me).

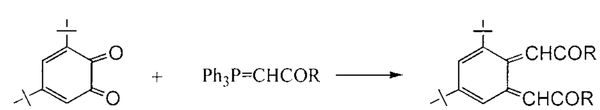


235 **236**



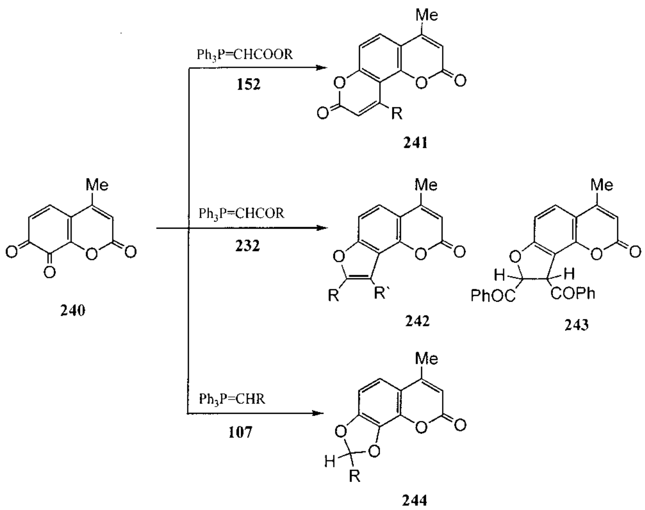
237 **238**

3,5-Di-*tert*-butyl-*o*-benzoquinone (**1**) reacts with ylides **232** (R = Me, Ph) in boiling benzene or ethanol to give 1,2-di-α,β-unsaturated ketones **239**.[155]

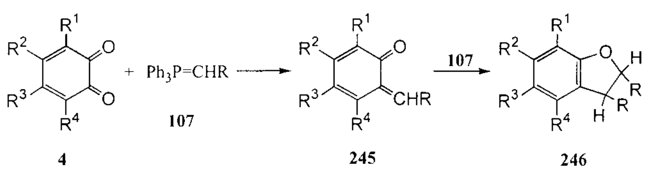


1 **232** **239**

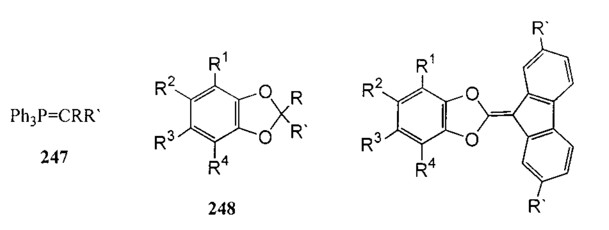
The reaction of 4-methylchromene-2,7,8-trione (**240**) with alkoxycarbonylmethylene(triphenyl)phosphoranes (**152**, R = Me, Et) in dichloromethane at room temperature gives the pyranocoumarines **241**. Also, *o*-quinone **240** reacts with phosphonium ylide **232** (R = Me) in boiling dichloromethane to produce the furocoumarins **242** (R = Me, R′ = H; R = Me, R′ = CH_2COMe), but in the case of ylide **232** (R = Ph), the products **242** (R = Ph, R′ = CH_2COPh) and **243** are afforded. When *o*-quinone **240** is allowed to react with ylides **107** (R = C_6H_4OMe-*p*, CH=CH_2, CH=CMe_2), the dioxolo compounds **244** are formed. The structure of adduct **242** (R = Me, R′ = CH_2COMe) was identified by X-ray analysis.[160]



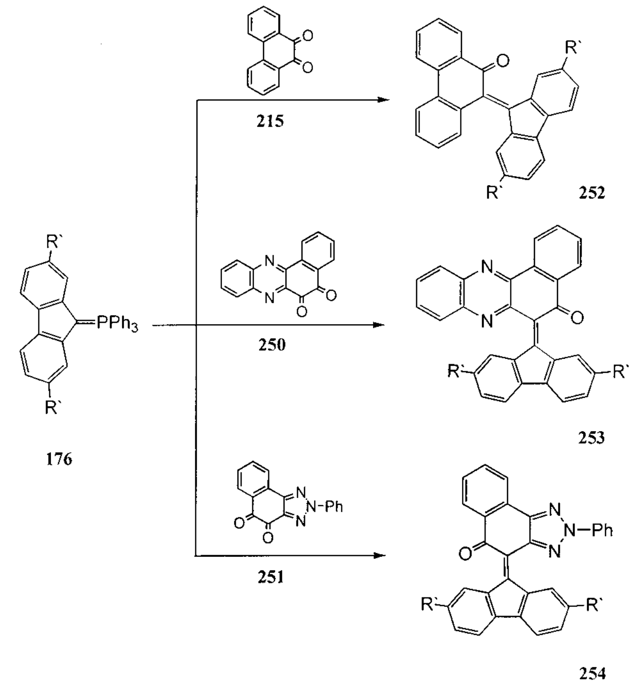
Phenanthrenequinone [**4,** R^1R^2 = R^3R^4 = $(CH)_4$] and naphthoquinone [**4,** R^1R^2 = $(CH)_4$, R^3 = R^4 = H] react with 1 mol equiv of benzylidene(triphenyl)-phosphorane (**107**, R = Ph, C_6H_4OMe-*p*, C_6H_4Br-*p*) to yield the stable *o*-quinone methanides **245**. While in case of 2 mol equiv, the dihydrofurans **246** are formed.[152,157,161]



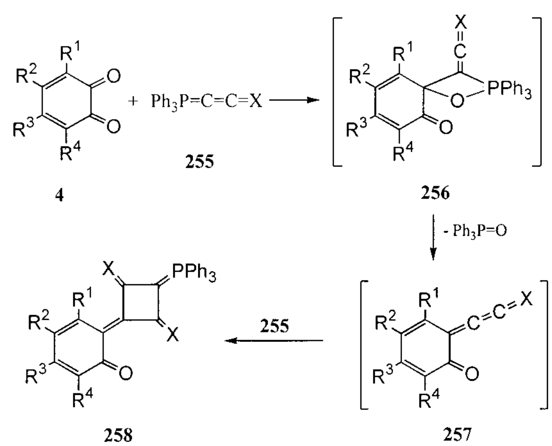
On the other hand, the reaction of methylene-(triphenyl)phosphoranes **247** (R = R′ = Ph; R = H, R′ = Ph) with substituted *o*-quinones **4** (R^1 = R^2 = R^3 = R^4 = Cl, Br; R^1 = R^3 = *t*-Bu, R^2 = R^4 = H; R^1 = R^4 = *t*-Bu, R^2 = R^3 = H) affords the corresponding 1,3-dioxole structures **248**. The reaction involves formation of an intermediate epoxide, which isomerizes to the dioxole derivatives.[152,162−164] Also, fluorenylidene(triphenyl)phosphoranes (**176**, R′ = H, Br) react with the same quinones **4** (R^1 = R^2 = R^3 = R^4 = Cl, Br; R^1 = R^3 = *t*-Bu, R^2 = R^4 = H) to form the 1,3-dioxole adducts **249**.[162,163]



Phenanthrenequinone (**215**), benzo[*a*]phenazine-5,6-dione (**250**), and 2-phenyl-2H-naphtho[1,2-*d*]triazole-4,5-dione (**251**) react with fluorenylidene(triphenyl)phosphoranes (**176**, R′ = H, Br) in benzene or toluene to yield the corresponding fluorenylidene derivatives **252** (R′ = H), **253** (R′ = H, Br), and **254** (R′ = H, Br), respectively.[157,165]

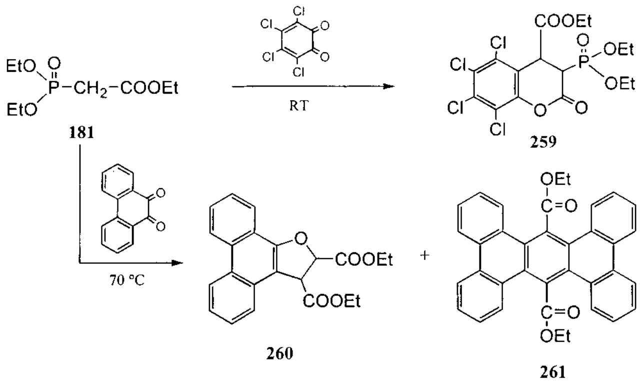


The reaction of *o*-chloranil **4** (R^1 = R^2 = R^3 = R^4 = Cl) and phenanthrenequinone **4** [R^1R^2 = R^3R^4 = $(CH)_4$] with active phosphacumulenes **255** (X = O, S) occurs by the [2 + 2]-cycloaddition of one carbonyl group in the quinones to the ylidic C−P bond of the ylides **255** to form the oxaphosphetanes **256** as an intermediate. The unstable ketenes **257** are formed by elimination of triphenylphosphine oxide, which add another molecule of **255** to produce the phosphoranylidenecyclobutanes **258**.[166]



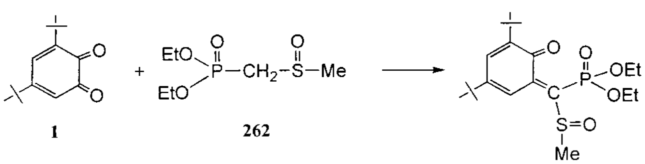
Phosphoranylidenecyclobutanes are also formed from the reaction of acenaphthenequinone,[166] benzo-[*b*]thiophene-2,3-dione,[140] and 3,4-diphenylcyclobutenedione[166] with active ylides **255**.

Wittig−Horner reagent **181** reacts with *o*-chloranil in 2:1 molar ratio in the presence of alcoholic sodium ethoxide at room temperature to give the phosphonate derivative **259**,[150] while phenanthrenequinone (**215**) reacts with the same phosphonate **181** at 70 °C for 8 h to yield 2,3-dicarbethoxyphenanthro[9,10-*b*]dihydrofuran (**260**) and the dimeric product **261**.[150]

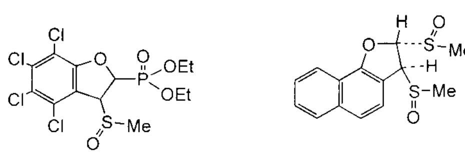


181 **259** **260** **261**

The reaction of α-phosphoryl sulfoxide **262** with 3,5-di-*tert*-butyl-*o*-benzoquinone (**1**) in sodium ethoxide solution at room temperature forms the quinonemethanephosphonate **263** in 63% yield.[167] Under the same experimental conditions, *o*-chloranil and *o*-naphthoquinone are reacted with phosphonium reagent **262** to give the dihydrofuran phosphonate **264** and *trans*-bis(methyl sulfoxide) coumaran **265**.[167]



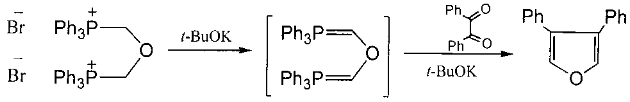
1 **262** **263**



264 **265**

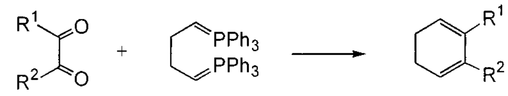
Several unsaturated cyclic compounds have been prepared by treatment of bis-phosphonium salts with a base in the presence of α-dicarbonyl compounds, through a double reaction, termed a bis-Wittig reaction.[168−173]

Benzil reacts with dimethyl ether α,α′-bis[triphenylphosphonium] dibromide (**266**) in *tert*-butyl alcohol in the presence of potassium *tert*-butoxide to give 3,4-diphenylfuran **267** in 30% yield.[168]



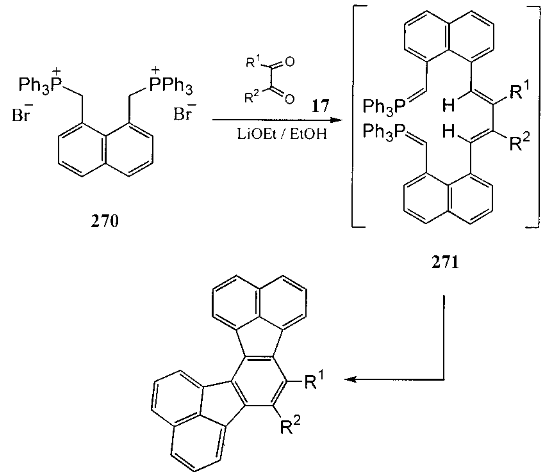
266 **267**

The saturated bis-ylide **268**, obtained from butan-1,4-bis[triphenylphosphonium] dibromide and potassium *tert*-butoxide, is fairly stable and reacts with α-diketones **17** [$R^1 = R^2 =$ Me; $R^1 =$ Me, $R^2 =$ Et; $R^1 =$ Ph, $R^2 =$ H; $R^1R^2 = (CH_2)_n$, $n = 2, 3, 4$] to produce 2,3-dialkyl-1,3-cyclohexadienes (**269**).[174]



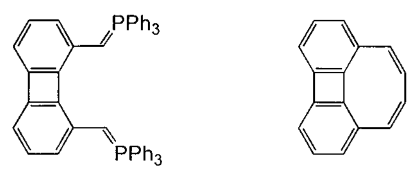
17 **268** **269**

An unusual reaction occurs when benzil (**17**, $R^1 = R^2 =$ Ph) and its *p*-substituent **17** ($R^1 = R^2 = C_6H_4$-Cl-*p*) react with bis-salt **270** in the presence of lithium ethoxide solution as a base to yield the cis−cis intermediate **271**. The polycycle **272** is formed from several oxidation steps of **271**.[175]



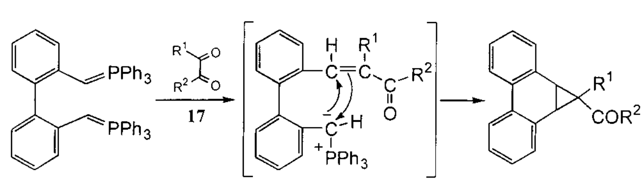
270 **271** **272**

Condensation of biphenylene-1,8-bismethylidenetriphenylphosphorane (**273**) with glyoxal (**17**, $R^1 = R^2 \simeq$ H) in tetrahydrofuran at 45 °C leads to the formation of cyclooctatetraene **274**.[176]



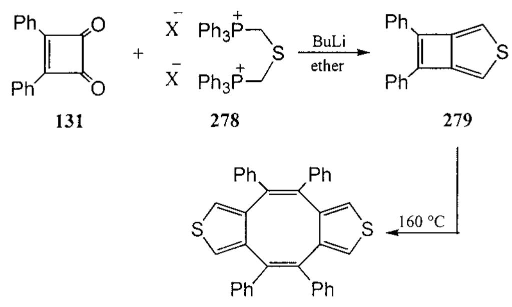
273 **274**

On the other hand, the reaction of bis-ylide **275** with biacetyl (**17**, $R^1 = R^2 =$ Me) and benzil (**17**, $R^1 = R^2 =$ Ph) in benzene or dioxane affords the intermediate carbonyl benzylidenephosphorane **276**, which undergoes an intramolecular Michael addition with elimination of triphenylphosphine to form the corresponding dibenzonorcaradiene derivatives **277**.[177]



275 **276** **277**

The reaction of diphenylcyclobutenedione (**131**) with dimethyl thioether-α,α′-bis[triphenylphosphonium] dichloride (**278**, X = Cl) in an ethereal solution of butyllithium as a base gives the bicyclo adduct **279** in low yield, which upon heating under nitrogen at 160 °C for 1 h affords the dimeric structure **280**.[168,178]

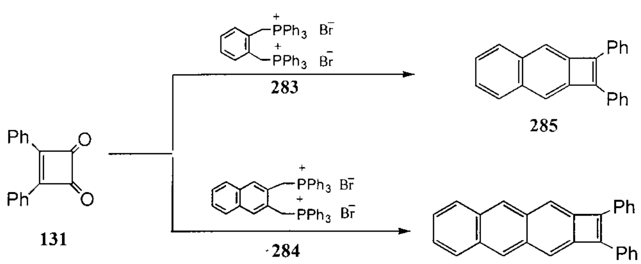


131 **278** **279** **280**

Similarly, 3,4-cyclobutanedione and benzocyclobutanedione react with bis-ylide **278** to form the corresponding adducts **281**[179] and **282**,[180,181] respectively.

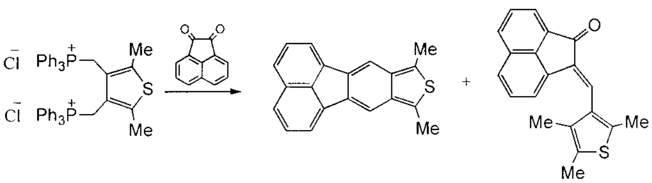
281 **282**

Bis-Wittig reaction of dione **131** with bis-salts **283** and **284** in the presence of lithium ethoxide as a base at 90 °C gives 1,2-diphenylnaphtho[*b*]cyclobutadiene (**285**) and 1,2-diphenylanthra[*b*]cyclobutadiene (**286**) in 20% and 16% yield, respectively.[182]



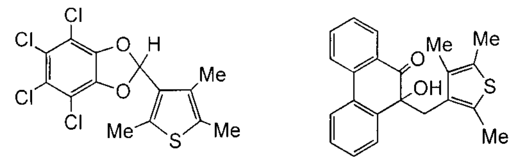
131 **283** **284** **285** **286**

Acenaphthenequinone reacts with 1,4-bisphosphonium salt **287** in dichloromethane in the presence of lithium hydroxide to afford the bis-Wittig product **288** in 24% yield with *o*-quinomethane derivative **289** in 4% yield.[183]



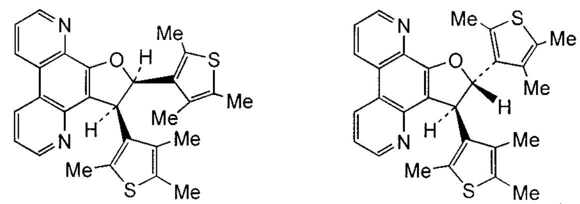
287 **288** **289**

By the same manner, *o*-chloranil and phenanthrenequinone react with bis-salt **287** to produce the dioxole derivative **290** and 10-hydroxy-10-(2,4,5-trimethyl-3-thenyl)phenanthren-9-one (**291**), respectively.[183]

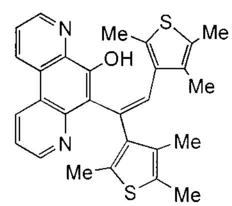


290 **291**

On the other hand, 4,7-phenanthroline-5,6-dione and the salt **287** are treated with aqueous lithium hydroxide to form the *cis*-**292** and *trans*-**293** isomers of bis-Wittig product, along with compound **294** in low yield.[183]

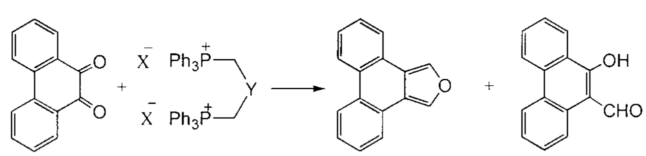


292 **293**



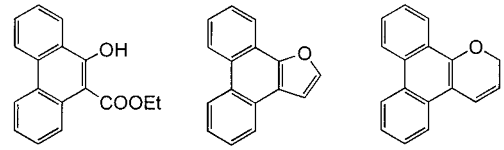
294

1,3-Bisphosphonium salt **295** (X = Br, Y = O) reacts with phenanthrenequinone (**215**) in dimethylformamide in the presence of lithium ethoxide to give **296** and the unexpected product **297**. Under the same



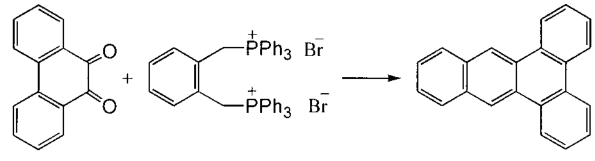
215 **295** **296** **297**

experimental condition, the salts **295** (X = Cl, Y = CO; X = Cl, Y = S; X = Br, Y = CH_2) with phenanthrenequinone afford the related compounds **298**, **299**, and **300**, respectively.[184]



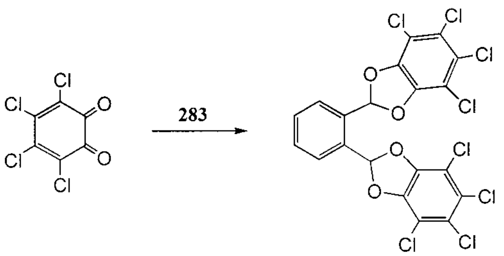
298 **299** **300**

o-Xylenebis(triphenylphosphonium bromide) (**283**) reacts with phenanthrenequinone (**215**) in dimethylformamide and in the presence of lithium ethoxide as a base to give the polycyclic aromatic compound **301**.[185] Also, *o*-naphthoquinone, acenaphthenequinone, and 4,5-dimethoxy-1,2-benzoquinone show similar behavior toward reaction with the same ylide **283** to



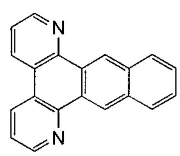
215 **283** **301**

yield the corresponding polycyclic hydrocarbons.[185,186] Meanwhile, *o*-chloranil reacts with bis-ylide **283** under the same experimental condition to produce the unexpected bis-benzodioxole derivative **302**.[185]



302

4,7-Phenanthroline-5,6-quinone undergoes bis-Wittig reaction with ylide **283** in the presence of lithium ethoxide to give naphtho[2,3-*f*][4,7]phenanthroline (**303**),[185] whereas in the presence of lithium hydroxide, phase-transfer catalysis gives, beside the polycyclic compound **303** (11% yield), 2,3-bis(*o*-tolyl)-2,3-dihydrofuro[2,3-*f*][4,7]phenanthroline (**304**) in 34% yield.[183]



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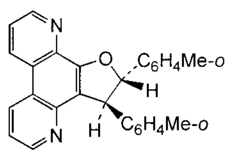
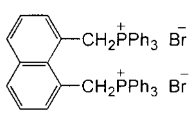


304

The reaction of 1,5-bis-phosphonium salt **270** with phenanthrenequinone and *o*-naphthoquinone in the presence of lithium ethoxide at room temperature affords the 1-(*o*-hydroxyaryl)acenaphthenes **305** and **306** in 49% and 6% yields, respectively.[184]



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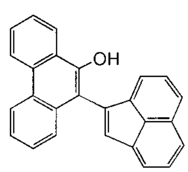

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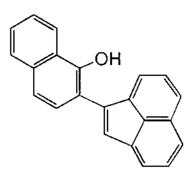
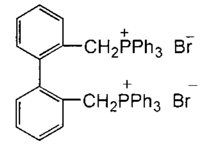


306

Treatment of phenanthrenequinone and 4,7-phenanthroline-5,6-dione with 1,6-bis-phosphonium salt **307** in dry dimethylformamide in the presence of lithium ethoxide solution forms 9-(*o*-hydroxyaryl)phenanthrenes **308** and **309**.[184]



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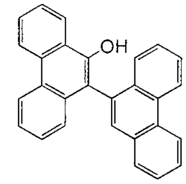

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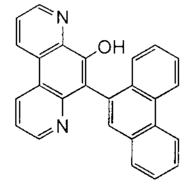
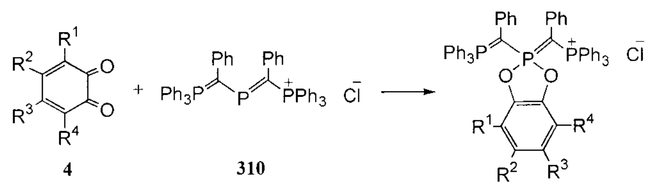


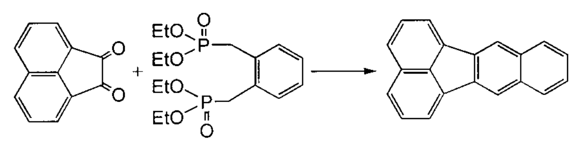
309

Reaction of bis(ylidyl)phosphonium chloride **310** with substituted *o*-quinones **4** [$R^1 = R^2 = R^3 = R^4 =$ Cl; $R^1 = R^3 =$ *t*-Bu, $R^2 = R^4 =$ H; $R^1R^2 = (CH)_4$, $R^3 = R^4 =$ H; $R^1R^2 = R^3R^4 = (CH)_4$] in dichloromethane at room temperature yields the corresponding bis(ylidyl)-1,3,2-dioxaphospholenium salts **311**.[187]



4 **310** **311**

Benzo[*k*]fluoranthene **313** has been obtained from the reaction of acenaphthenequinone with tetraethyl *o*-xylylenediphosphonate **312** via the Horner reaction.[188]

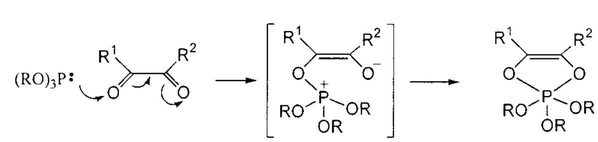


312 **313**

IX. Reactions with Phosphite Esters

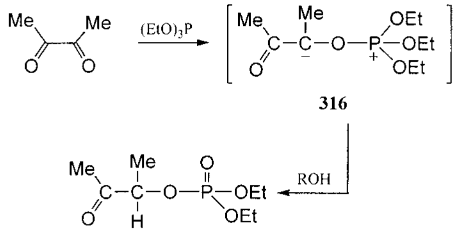
The reactions of alkyl phosphites with α-dicarbonyl compounds have been investigated.[189,190] In some of these systems, the phosphorus atom attacks the carbon of the carbonyl function group; however, in others the phosphorus attacks the oxygen of the carbonyl to produce five-memberd cyclic oxyphosphoranes.

α-Diketones **17** ($R^1 = R^2 =$ Me, Ph; $R^1 =$ Me, Ph, $R^2 =$ Et; $R^1 =$ Ph, $R^2 =$ 1-azulenyl; $R^1 = R^2 = CF_3$, 2-furyl) react with trialkyl phosphites to give 1:1 adducts of cyclic oxyphosphorane structure **315**.[191−202] The mechanism involves nucleophilic attack on oxygen as the first step of a biphilic process leading to the phosphonium enolate intermediate **314**, which very readily cyclizes to the final product **315**.



17 **314** **315**

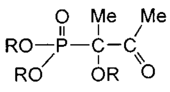
Birum and Dever[203] reported that the reaction of trialkyl phosphites with biacetyl in proton-donating solvent leads to the phosphate **317**, which confirms the intermediate formation of dipolar ion **316**.



316

317

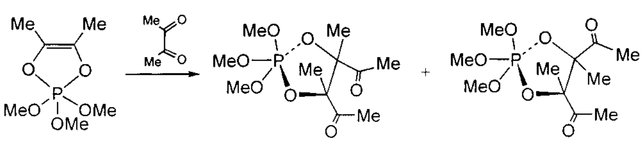
On the other hand, Kukhtin and co-workers[204−207] showed that the reaction of biacetyl with tertiary phosphites furnishes different adducts believed to be derived from the cyclic oxyphosphoranes **315** and to have structure similar to **318**.



318

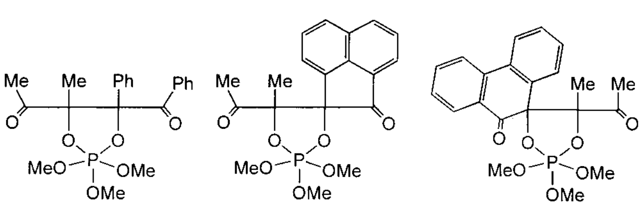
The cyclic unsaturated pentaoxyphosphoranes **315** are quite stable and sensitive to moisture. However, on heating they regenerate the starting materials.[208] They react very rapidly with water,[19,209] with dry oxygen,[191,193,210] and with a variety of reagents, such as bromine[191,211] and ozone.[191,212,213]

The nucleophilic additions of 1,3,2-dioxaphospholenes **315** to a large variety of α-dicarbonyl compounds give rise to new families of oxyphosphoranes. Thus, biacetyltrimethyl phosphite 1:1 adduct **319** reacts slowly with a second molecule of biacetyl and yields two diastereomeric forms of 2:1 adduct, having a cyclic saturated oxyphosphorane structure with the new 1,3-dioxaphospholane.[16,198,214] These two forms are the meso form (**320a**, 80% yield) and the racemic form (**320b**, 20% yield).



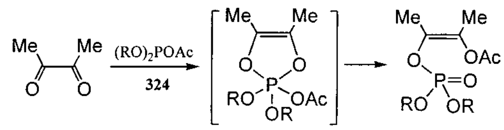
319 *meso*-**320a** *racemic*-**320b**

Also, it was found that the phospholene **319** reacts with benzil,[215] acenaphthenequinone,[16] and phenanthrenequinone,[215] yielding the corresponding cyclic saturated oxyphosphoranes **321**, **322**, and **323**, respectively.



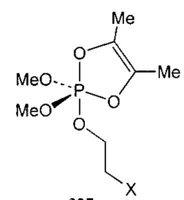
321 322 323

The reaction of biacetyl with acyl phosphites **324** (R = Et, Bu) proceeds through an intermediate with a pentacoordinate phosphorus atom (**325**), which has been demonstrated by ^{31}P NMR.[216] However, the presence of the anionoid acetyl group makes dioxaphospholenes **325** unstable, and they react further via the mechanism of the second stage of the Arbuzov rearrangement with ring opening and the formation of α,α-endiol phosphates **326**.[216,217]



325 326

The pentaoxyphosphoranes **327** (X = OMe, OEt, CH_2OMe, CH_2Me), **328** (X = O, CH_2), **329** (X = OMe, OEt, CH_2OMe, CH_2Me), and **330** (X = O, CH_2) were synthesized from the corresponding phosphite triester (P^{III}) compounds via reaction with biacetyl.[218−220] A variable-temperature ^{13}C NMR accompanied by a high-resolution ^{1}H NMR conformational analysis on these monocyclic pentacoordinated (P^{v}) trigonal bipyramidal (TBP) compounds **327**−**330** has revealed the influence of the conformational transmission effect on the barriers to pseudorotation.[218−220]



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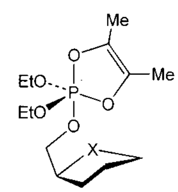

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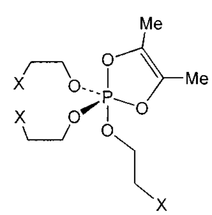

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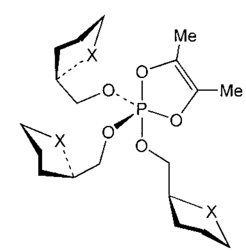
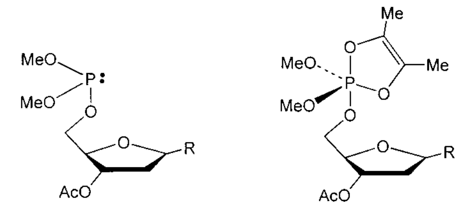


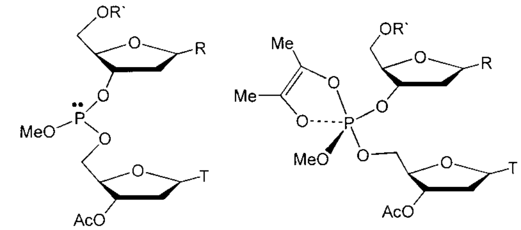
330

Also, Koole et al. reported[218,220−223] an additional study of the conformational transmission effect in another P^{v} TBP model systems related to compounds **327**−**330**.

A set of nucleotide analogues containing a stable trigonal bipyramidal phosphorus (P^{v} TBP) moiety (**332**, R = thymidyl, adenosyl, N^4-acetylcytidyl; and **334**, R = T = thymidyl, R′ = Ac, trityl; R = H, R′ = Ac, trityl) has been prepared from the corresponding phosphite triester (P^{III}) nucleotides **331** and **333** via reaction with biacetyl.[221] The ^{31}P NMR clearly confirmed that the phosphites **333** exist as a mixture of two diastereoisomers, but for the phosphites **334**, it was observed that the ^{31}P NMR spectrum consists of a single line. This proves that stereomutation around the P^{v} TBP is rapid on the NMR time scale.[222,223] The impact of conformational transmission on the molecular structure of the model systems **332** and **334** in an unequivocal way has been studied with 300- and 500-MHz ^{1}H NMR.[221]

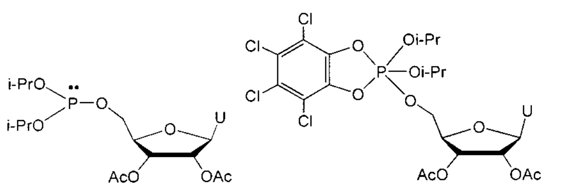


331 332



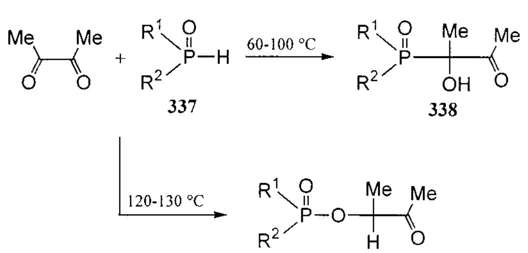
333 334

Recently, Zhao and Zhou[224] synthesized 2′,3′-di-*O*-acetyluridine 5′-oxyphosphorane **336** from the reaction of 2′,3′-di-*O*-acetyluridine 5′-diisopropyl phosphite (**335**) with an equivalent amount of tetrachloro-*o*-benzoquinone at room temperature for 10 min. The oxyphosphorane **336** proved to be stable enough to study its structure by ^{1}H NMR, ^{13}C NMR, FD-MS, and elemental analysis.



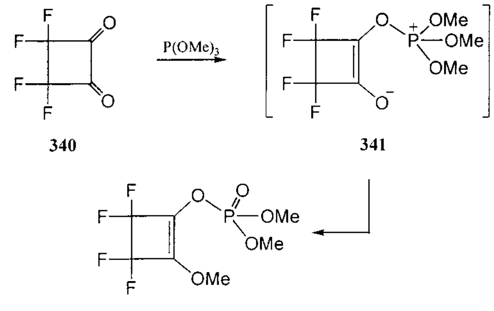
335 336

Dialkyl phosphites react with α-diketones to give the α-hydroxyphosphonates or their isomers, the enol phosphate esters, depending on the reaction condition.[225] For example, biacetyl reacts with dialkyl phosphites **337** ($R^1 = R^2 =$ O-alkyl) and *O*-alkyl alkylphosphonates **337** (R^1 = OEt, OPr, O-*i*-Pr; R^2 = Et) at moderate temperature to give the α-hydroxy derivatives **338**, whereas compounds **339** are formed at about 130 °C.[226,227]



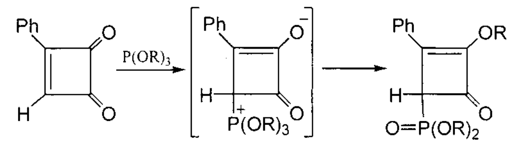
337 338 339

Tetrafluoro-1,2-cyclobutanedione (**340**) undergoes an addition reaction with trimethyl phosphite to produce the methyl ether of *o*-quinol phosphate **342** through the intermediate dipolar ion **341**.[228]



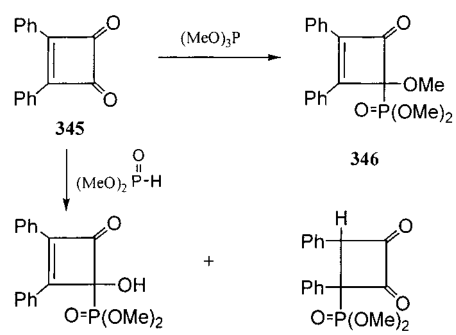
340 341 342

On the other hand, the condensation of phenylcyclobutenedione (**343**) with phosphite esters yields 1-alkoxy-3-dialkylphosphono-4-oxo-2-phenylcyclobutene (**344**) on the bases of the spectral evidence.[229]



343 344

Diphenylcyclobutenedione (**345**) in neat trimethyl phosphite is allowed to stand 3 days at room temperature or be heated for 2 h at 80 °C to form the 1,2-adduct **346** in quantitative yield.[230]

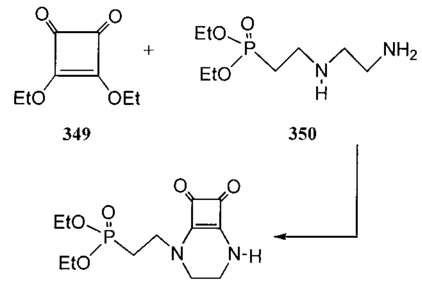


345 346 347 348

Treatment of dione **345** with dimethyl phosphite at 80 °C leads to the formation of two adducts identified as the 1,2-adduct **347** and the 1,4-adduct **348**.[230] The structural assignments are based on complete spectral and analytical data as well as the fact that the product **347** is converted quantitatively to **346** on warming with trimethyl phosphite.

3,4-Diethoxy-3-cyclobutene-1,2-dione (**349**) reacts with (phosphonoethyl)ethylenediamine (**350**) in boiling ethanol solution to give the phosphonic acid diethyl ester **351**.[231]

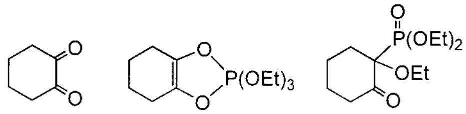
The reactivity of trialkyl phosphites with 1,2-cyclohexanedione (**352**) was investigated by Kukhtin and co-workers.[232] When cold, triethyl phosphite reacts with 1,2-cyclohexanedione (**352**), yielding the adduct **353** together with triethyl phosphate and diethyl ethylphosphonate. On the other hand, diethyl 1-ethoxy-2-oxocyclohexylphosphonate **354**, triethyl phosphate, and diethyl ethylphosphonate with a



349 350

351

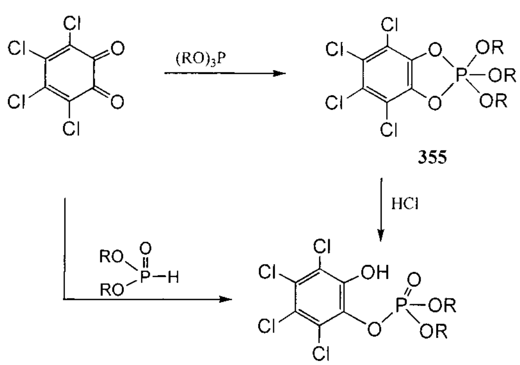
small amount of the phospholene **353** are obtained when the reaction was repeated with heat.[232]



352 353 354

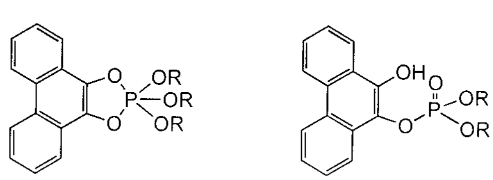
Generally, trialkyl phosphites react with *o*-quinones to form 1:1 adducts as cyclic structures containing pentavalent phosphorus.

The reaction of trialkyl phosphites with *o*-chloranil takes place in benzene solution at 20 °C to give the corresponding 1,3,2-dioxaphospholenes **355**,[233] which are converted into tetrachlorocatechol dialkyl phosphates **356** by means of hydrogen chloride. The same phosphate esters **356** are also obtained from the reaction of *o*-chloranil with dialkyl phosphites.[84,233−235]



356

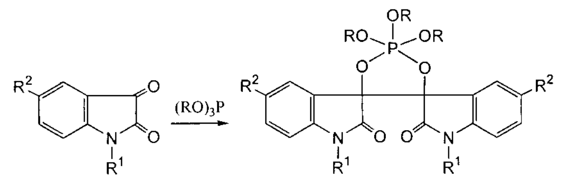
9,10-Phenanthrenequinone reacts with trialkyl phosphites in benzene solution to yield the unsaturated pentaoxyphosphorane adducts **357**.[191,192] The crystal and molecular structure of phosphorane **357** (R = *i*-Pr) has been determined by X-ray analysis.[236] When the above reaction takes place in the presence of acetic acid, the *o*-quinol monophosphates **358**,[237] which also formed from the reaction of phenanthrenequinone with dialkyl phosphites,[238] are obtained.



357 358

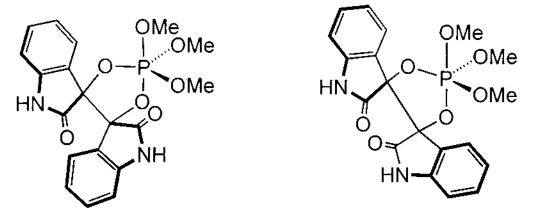
1,3,2-Dioxaphospholenes are formed when trialkyl phosphites react with 1,2-naphthoquinone,[233,239] 4-triphenylmethyl-1,2-benzoquinone,[240] 4,7-phenanthroline-5,6-quinone,[241] 3,5-di-*tert*-butyl-1,2-benzoquinone,[242] 2-phenyl-2H-naphtho[1,2-*d*]triazole-4,5-dione,[243] and 4,5-pyrenequinone.[233]

Trialkyl phosphites react with isatins (**359**) in benzene solution under nitrogen at room temperature to afford the 1:2 adducts as cyclic saturated pentaoxyphosphoranes **360**.[244−248]



359 360

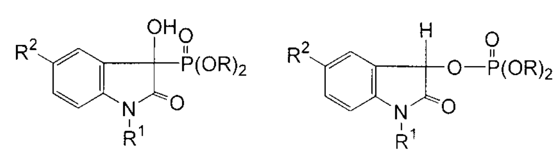
The presence of two chiral carbons in the pentaoxyphosphorane structure gives rise to the possibility of the existence of *meso*-**360a** and *d*,*l*-diasteriomers **360b**,[247] which has been confirmed in solution on the basis of ^{31}P and ^{1}H NMR spectroscopy.[247]



meso-**360a** *d, l*- **360b**

Similarly, acenaphthenequinone and 5,6-dihydrocyclopent[*fg*]acenaphthylene-1,2-dione[249] react with trialkyl phosphites to give the corresponding 2:1 adducts.

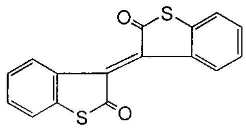
The reaction of dialkyl phosphites with isatins **359** (R^1 = H, Me, COMe; R^2 = H, Me) produces the corresponding dioxindole-3-phosphonic esters **361**.[73,244,250,251] While, Timmler[252] reported in a process patent that the reaction of isatin with dialkyl phosphites affords the dioxindolyl phosphate **362**.



361 362

Benzo[*b*]thiophene-2,3-dione reacts in a manner different from that noted with other α-diketones, undergoing deoxygenative dimerization in the presence of trialkyl phosphites to yield isothioindigo **363**. The phosphate products **364** are taken by the reaction with dialkyl phosphites in benzene solution at room temperature.[253]

Naphtho[2,1-*b*]furan-1,2-dione (**365**) reacts with trialkyl phosphites in benzene at room temperature to give about 85% yield of 2:1 adducts as pentaoxyphosphoranes (examined by ^{31}P NMR), which upon



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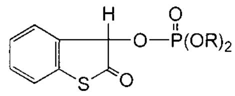
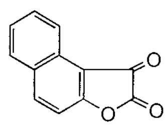


364

heating in absolute alcohols afford the unexpected products **366**.[254]



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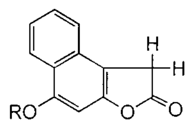
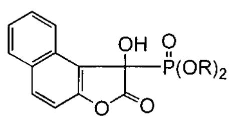


366

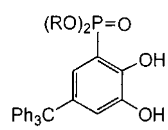
Dialkyl phosphites react with the same quinone **365** in boiling benzene for 12 h[244,250] or at room temperature for 10 min in the presence of aluminum oxide as a catalyst[251] to form the α-hydroxyphosphonates **367**.



367

Also, α-hydroxyphosphonates are produced from the reaction of dialkyl phosphites with acenaphthenequinone,[255] aceanthrenequinone,[255] and 5,6-dihydrocyclopent[*fg*]acenaphthylene-1,2-dione[249,251] in benzene solution.

4-Triphenylmethyl-*o*-benzoquinone and 3,5-di-*tert*-butyl-*o*-benzoquinone differ from other *o*-quinones in their reaction with dialkyl phosphites, since they give the corresponding 1:1 adducts formulated as the phosphonates **368**[240] and **369**[242] respectively.



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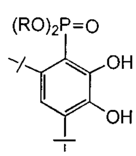
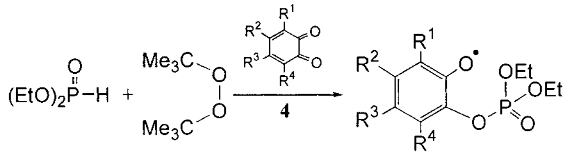


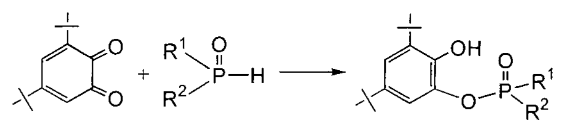
369

Treating diethyl phosphite with *tert*-butyl peroxide in toluene generates phosphonyl radical, which reacts with *o*-benzoquinones **4** ($R^1 = R^3 =$ *t*-Bu, $R^2 = R^4 =$ H; $R^1 = R^4 =$ *t*-Bu, $R^2 = R^3 =$ H; $R^1 =$ *t*-Bu, $R^2 = R^4 =$ H, $R^3 =$ OMe; $R^1 =$ *t*-Bu, $R^2 = R^3 =$ H, $R^4 = NO_2$; $R^1 =$ *t*-Bu, $R^2 = R^4 =$ H, $R^3 = CPh_3$) to yield the corresponding phenoxy radicals **370** (ESR).[256]



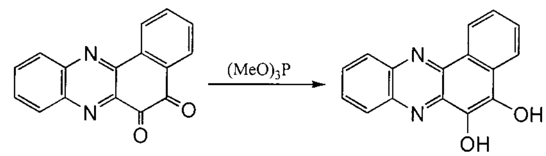
370

The reaction of 3,5-di-*tert*-butyl-*o*-benzoquinone with phosphoric acids **371** ($R^1 = R^2 =$ OH; $R^1 =$ OH, $R^2 =$ O-hexadecyl) affords the phosphorylated pyrocatechols **372**.[257]



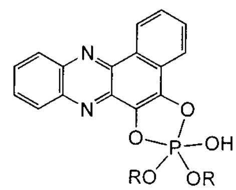
371 372

Mustafa et al.[238] showed that trimethyl phosphite affects reduction of benzo[*a*]phenazine-5,6-dione (**250**) to yield 3,4-dihydroxy-1,2-benzophenazine (**373**).



250 373

The addition of dialkyl phosphites to benzo[*a*]phenazine-5,6-dione (**250**) depends on experimental conditions.[238] When the reaction is carried out at room temperature, colorless 1:1 adducts believed to have structure **374** or **375** are isolated. In boiling benzene, the same reaction affords a mixture of **376** and **377**.



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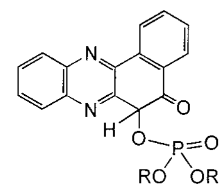

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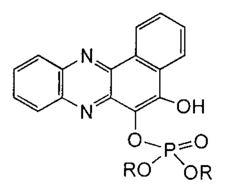

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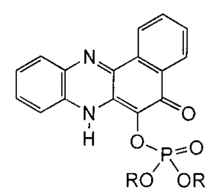
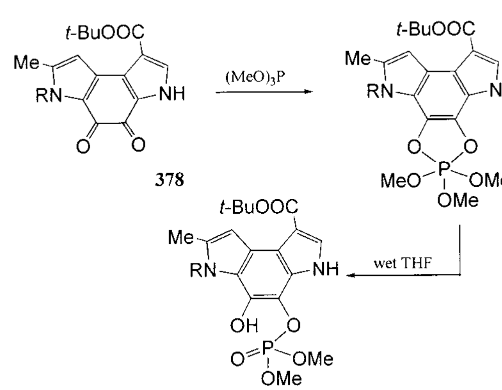


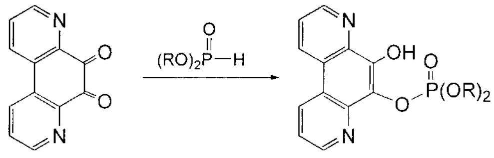
377

Reduction of *o*-quinones **378** (R = H, SO_2Ph) using trimethyl phosphite in benzene gives the cyclic oxyphosphoranes **379**, which are rapidly hydrolyzed in wet tetrahydrofuran to a single phenolic phosphate ester **380**.[258]



378 379 380

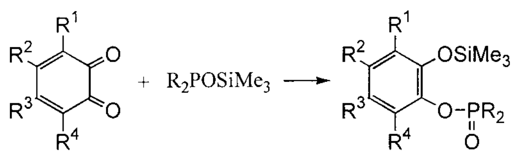
4,7-Phenanthroline-5,6-quinone reacts with dialkyl phosphites in boiling benzene to form colorless crystals of the corresponding *o*-quinolmonophosphate **381**.[241]



381

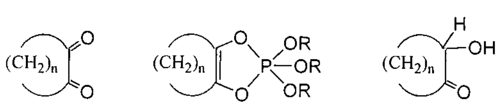
Similarly, furil,[105] 1,2-naphthoquinone,[84,251,259] and 2-phenyl-2H-naphtho[1,2-*d*]triazole-4,5-dione[243] react with dialkyl phosphites to produce the corresponding phosphates.

The reaction of phosphorus trimethyl silyl esters **382** (R = OMe, OEt, O-*i*-Pr, OPh) with substituted *o*-quinones **4** [$R^1 = R^2 = R^3 = R^4 =$ Cl; $R^1 = R^3 =$ *t*-Bu, $R^2 = R^4 =$ H; $R^1R^2 = (CH)_4$, $R^3 = R^4 =$ H; $R^1R^2 = R^3R^4 = (CH)_4$] gives 2-trimethylsilyloxyphenyl phosphoric acid derivatives **383**.[84,260] The structure of **383** [R = O*i*-Pr, $R^1R^2 = R^3R^4 = (CH)_4$] was confirmed by a single-crystal X-ray analysis.[84]



4 382 383

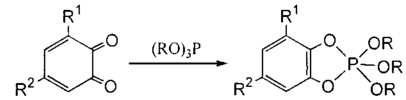
Treatment of cycloalkanediones **384** ($n = 5, 6$) with trialkyl phosphites yields the dioxaphospholenes **385**,[261] whereas the cycloalkanediones **384** ($n = 11, 12, 13$) with triethyl phosphite in the presence of potassium hydroxide give the corresponding acyloins **386**.[262]



384 385 386

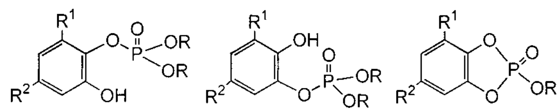
A spectrophotometric kinetic study of the reactions of alkyl phosphites with aliphatic α-diketones, cyclic α-diketones, and *o*-quinones has been performed.[195,263−266] The rate of reaction increases in the following series of aliphatic α-diketones: R = Me > Et > *n*-Pr > *i*-Pr > *i*-Bu, while in case of cyclic α-diketones and *o*-quinones, the rate constant decrease with increasing ring size.

o-Quinones in wood pulp react with trialkyl phosphites to form the cyclic phosphite esters.[267−270] Their detection has become possible in solid pulp and soluble lignin samples[271−274] by oxyphosphorylation followed by elemental analysis of the phosphorus content of the treated pulps by ^{31}P NMR chemical shift, which shows a signal at about −46 ppm.[271] Treatment of *o*-quinones **387** ($R^1 = R^2 =$ H; $R^1 =$ Me, $R^2 =$ H; $R^1 =$ Me, $R^2 =$ OMe; $R^1 = R^2 =$ *t*-Bu) present in wood pulp[267−270] and lignin[271,272] with trialkyl phosphites (R = Me, *i*-Pr) at room temperature affords the expected cyclic oxyphosphorane adducts **388**,[268,271,272] which are very sensitive to trace amount



387 388

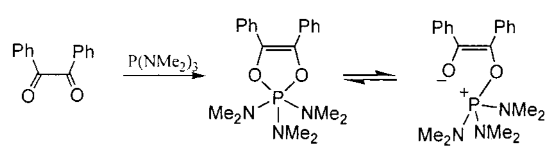
of water usually present in pulp and/or lignin samples. So the signal at −46 ppm disappeared with the simultaneous formation of a new signal at about −2 ppm, corresponding to the open ring products that are formed as two sets of isomers **389** and **390**, with total yield about 70%, and trace amounts of the cyclic phosphite ester **391** derived from compound **388**.



389 390 391

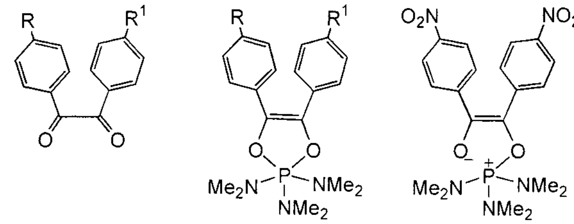
X. Reactions with Hexamethylphosphorus Triamide and Phosphoramidites

A series of organophosphorus compounds has been prepared by condensation of hexamethylphosphorus triamide with α-dicarbonyl compounds.[275−282] The phosphorus of hexamethylphosphorus triamide is added to the oxygen of benzil to give a 1:1 adduct. Burgada[280,282] assigned that 1:1 adduct as pentavalent phosphorus **392**, while Ramirez et al.[277] showed that the resulting 1:1 adduct can be isolated in two crystalline forms, one with pentavalent phosphorus (**392**) and the other with tetravalent phosphorus (**393**) according to ^{31}P NMR chemical shift.



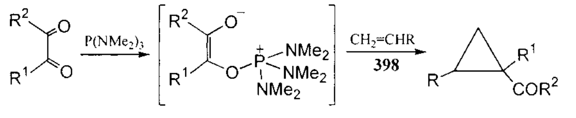
392 393

Denney et al.[283] studied the ^{31}P and ^{13}C NMR spectra for a solution of the 1:1 adducts produced from the reaction of hexamethylphosphorus triamide with a series of substituted benzils **394** ($R = R^1 =$ Me, OMe, F, NO_2; R = H, $R^1 =$ Cl). They found that the 1:1 adducts ($R = R^1 =$ Me, OMe) are phosphoranes **395** by negative ^{31}P chemical shift and the strong $^3J_{PC}$ coupling to the *ipso*-carbons in the ^{13}C NMR spectra. However, in the 1:1 adduct ($R = R^1 = NO_2$), the ^{31}P chemical shift is positive and the $^3J_{PC}$ coupling is lost, indicating the ionic species **396**.[283]



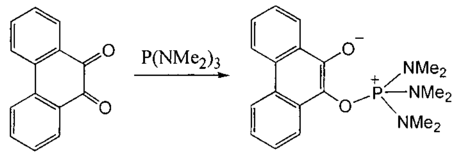
394 395 396

Treatment of α-diketones **17** (R^1 = COOEt, Ph; R^2 = OEt, Ph, OMe) with phosphorus triamide gives phosphonium betaine intermediates **397**, which are then stirred with monosubstituted ethene **398** (R = COOMe, Ac, CN) to form the corresponding polysubstituted cyclopropanes **399**.[284]



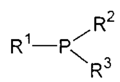
17 **397** **399**

9,10-Phenanthrenequinone reacts with hexamethylphosphorus triamide in dichloromethane at 0 °C to afford the stable product triaminooxyphosphonium dipolar ion **400** in the crystalline form;[277−279] this is due to the phenanthrene backbone, which can delocalize the negative charge.

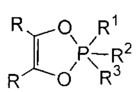


400

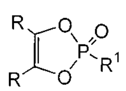
Biacetyl reacts with phosphoramidites **401** (R^1 = R^2 = OEt, OPr, R^3 = NEt_2, NHAc; R^1 = OPr, R^2 = NEt_2, R^3 = Ph, Me) in inert atmosphere at room temperature to yield the corresponding phosphoranes **402**,[285−288] which upon heating give the phosphates **403** (R^1 = OEt, OPr).[285,289] The reaction of benzil with *N*-acetylphosphoramidite **401** (R^1 = R^2 = OEt, R^3 = NHAc) at room temperature produces the phosphate **403** (R^1 = OEt).[285]



401

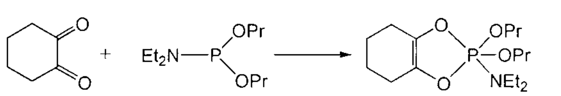


402



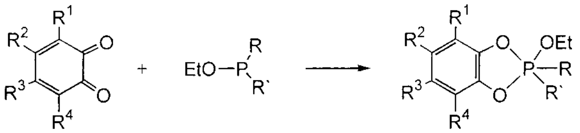
403

1,2-Cyclohexanedione reacts with phosphoramidite **404** below 10 °C to give 30% yield of the aminophosphorane **405**.[286]



404 **405**

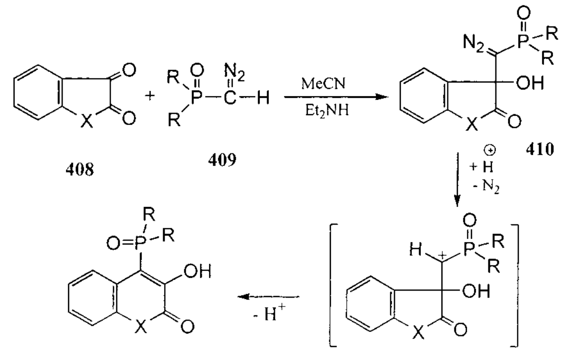
The reaction of substituted *o*-benzoquinone **4** [R^1 = R^2 = R^3 = R^4 = Cl, Br; R^1R^2 = R^3R^4 = $(CH)_4$; R^1 = R^2 = H, R^3 = R^4 = OMe] with phosphoramidites **406** (R = OEt, NEt_2; R′ = NEt_2, NHEt, NHPh, NHC_6H_4-Me-*p*, NHC_6H_4OMe-*p*) forms the cyclic adducts **407**.[290,291]



4 **406** **407**

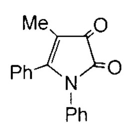
XI. Reactions with α-Diazoalkyl Phosphorus Compounds

α-Diketones **408** (X = CMe_2, CPh_2, NH, NMe, NOH, NOAc, NAc, O) react with (diazomethyl)diphenylphosphine oxide (**409**, R = Ph) and dimethyl diazomethyl phosphonate (**409**, R = OMe) in the presence of a base catalyst to form α-oxodiazoaldols **410**. The diazo compounds **410** undergo ring enlargment via the corresponding carbonium ions **411** when decomposed with ethereal hydrogen chloride to give **412**.[292,293]

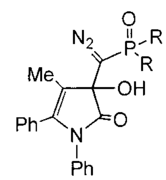


408 **409** **410** **411** **412**

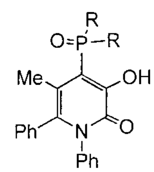
By the same manner, 1,5-diphenyl-4-methyl-2,3-pyrrolinedione (**413**) reacts with phosphoryldiazoalkenes **409** (R = Ph, OMe) to yield diazomethyl-2-pyrrolinone **414**, which is then decomposed with ethereal hydrogen chloride to form 4-diphenyl- and 4-dimethoxyphosphoryl-3-hydroxy-5-methyl-1,6-diphenyl-2-pyridone (**415**).[292]



413

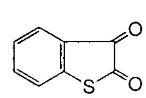


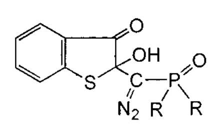
414



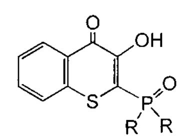
415

On the other hand, benzo[*b*]thiophene-2,3-dione with phosphoryldiazoalkanes **409** (R = Ph, OMe) affords the 2-addition products **416**, which are converted to **417** by ring expansion.[292]



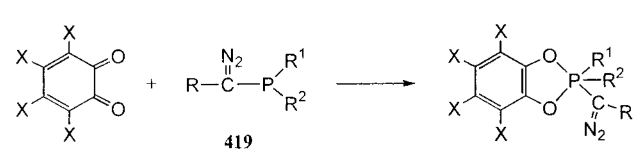


416



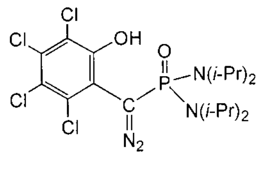
417

The (diazoalkyl)phosphines **419** [R = CMe_3, R^1 = R^2 = $CHMe_2$, CMe_3, NEt_2, N(*i*-Pr)$_2$] undergo [4 + 1]-cycloaddition reactions with tetrahalo-*o*-benzoquinones (**418**, X = Cl, Br) to furnish (diazoalkyl)-phosphoranes **420**.[294]

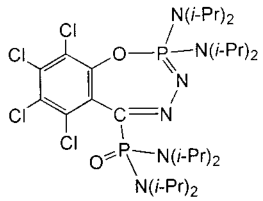


418 **419** **420**

When a stoichiometric amount of *o*-chloranil was added at −78 °C to a tetrahydrofuran solution of **419** [R = $SiMe_3$, R^1 = R^2 = N(*i*-Pr)$_2$], a mixture of oxophosphoranyldiazo derivative **421** and the seven-memberd heterocycle **422** are formed in 30% and 50%



421



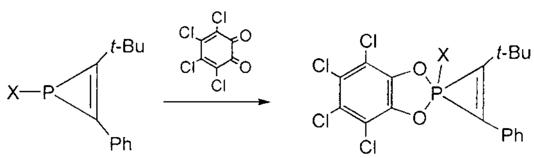
422

yield, respectively.[282] The structure of compounds **420** [X = Br, $R^1 = R^2 = N(i\text{-}Pr)_2$], **421**, and **422** have been characterized by single-crystal X-ray diffraction studies.[294,295]

XII. Reactions with Heterocyclic Phosphorus Compounds

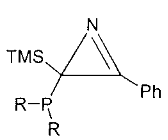
The chemistry of cyclic organic compounds containing a phosphorus atom is a rapidly growing field drawing much attention in recent times due to their preferential toxicity for cancer cells[296−299] when released in tissues and their potential applications in the technical fields, for example, as pesticides[300] and herbicides.[301]

1-Halo- and 1-cyano-1*H*-phosphirenes (**423**, X = F, Cl, Br, CN) react with *o*-chloranil in ether by oxidative addition at phosphorus to furnish the pentacoordinated phosphirenes **424**.[302]



423 **424**

On the other hand, the 2-phosphino-2*H*-azirine **425** (R = Cy_2CN) is added to *o*-chloranil to produce the eight-membered heterocycle **426** with 60% yield. Its structure was detected by X-ray crystallography.[303]



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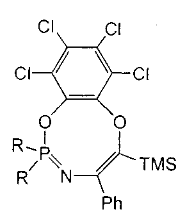
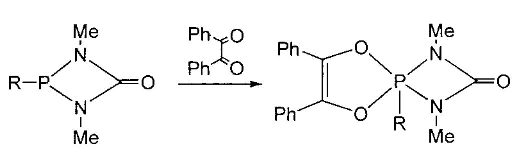


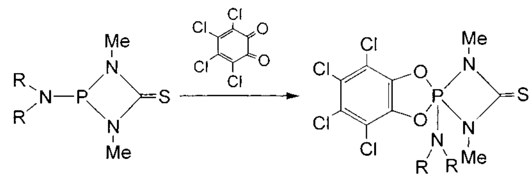
426

The cyclic phosphines **427** (R = NMe_2, OMe)[304] react with benzil to form the corresponding spirophosphranes **428**.[305] The structures of these products were confirmed by ^1H NMR studies with variable temperature.



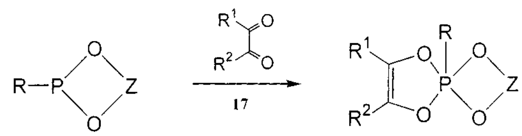
427 **428**

Oxidation reaction of diazaphosphetidinethiones **429** (R = Me, C_6H_{11}, Ph) with *o*-chloranil in dichloromethane (−10 to 40 °C) produces spirophosphorane adducts **430**.[306,307] Compound **430** (R = C_6H_{11}) was characterized by X-ray analysis.[307]



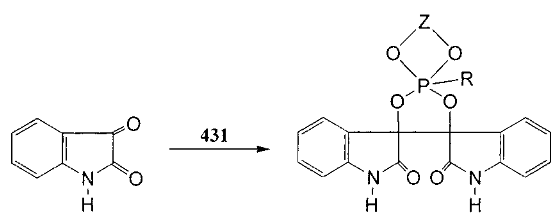
429 **430**

The reaction of cyclic phosphorus compounds **431** [R = OMe, NMe_2, $OSiMe_3$; Z = CH_2CH_2, CHMeCHMe, CMe_2CMe_2, CH_2CHMe, $(CH_2)_3$, $CH_2CMe_2CH_2$, CH_2CH_2CHMe, *o*-C_6H_4] with biacetyl (**17**, $R^1 = R^2 = Me$) and benzil (**17**, $R^1 = R^2 = Ph$) affords the phosphoranes **432**.[308−310] Similarly, phenanthrenequinone reacts with **431** (R = OMe, Z = CH_2CH_2) to yield the corresponding phosphorane.[310]



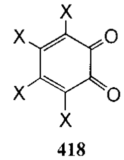
431 **432**

Isatin reacts with cyclic phosphites **431** [R = OEt, OBu, OPh, NEt_2; Z = CH_2CH_2, $(CH_2)_3$, *o*-C_6H_4] in dichloromethane or benzene under dry conditions to give the pentacoordinate 2:1 adducts **433**. The isomeric composition of **433** depends on the original phosphorus compound.[311]

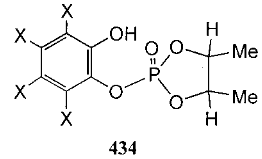


433

Treatment of phosphite **431** (R = $OSiMe_3$, Z = CHMeCHMe) with tetrahalo-*o*-benzoquinones (**418**, X = Cl, Br) yields the phosphates **434**.[308]

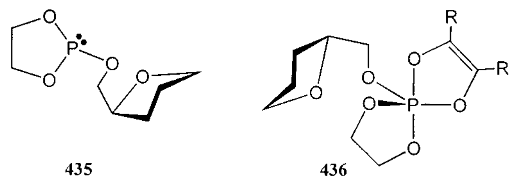


418



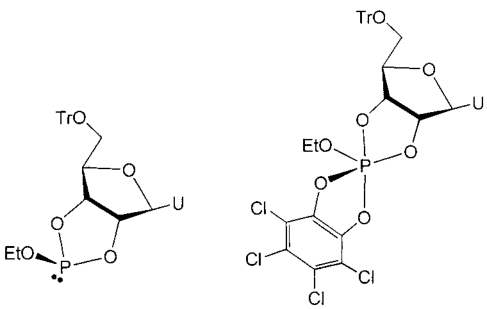
434

2-(Tetrahydrofurfuryloxy)-1,3,2-dioxaphospholane (**435**) reacts with biacetyl and benzil in anhydrous diethyl ether at 0 °C to form the corresponding spirophosphoranes **436** (R = Me, Ph).[218] The ^1H NMR studies with variable temperature of the P^v TBP model compounds **436** show that axial location of the tetrahydrofurfuryl group results in an unfavorable diequatorial arrangement of one of the five-membered fragments.[312] In these spirophosphoranes, the tetrahydrofurfuryl group is likely to act as the pivot,[312−314] which occupies an equatorial position.



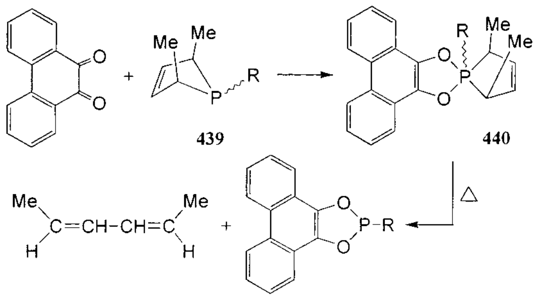
435 436

Uridine 2′,3′-cyclic phosphite **437** (Tr = trityl) reacts with an equivalent amount of tetrachloro-1,2-benzoquinone in methylene chloride at −40 °C to yield the analytical pure uridine 2′,3′-cyclic phosphorane **438**. This oxyphosphorane is the first synthetic model containing a ribonucleoside residue, for the hydrolysis of RNA and the enzymatic reactions involving RNase and cyclic phosphatase.[315]



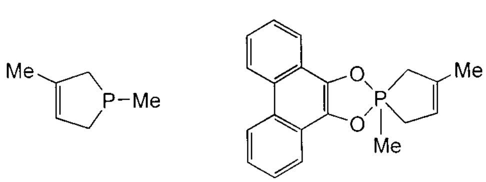
437 438

Reaction of phospholenes **439** (R = *cis*-, *trans*-Me, Ph) with phenanthrenequinone affords quantitative yields of compounds **440**, which upon heating give a mixture of the phosphoranes **441** and the trans,trans-isomer of **442**.[316]



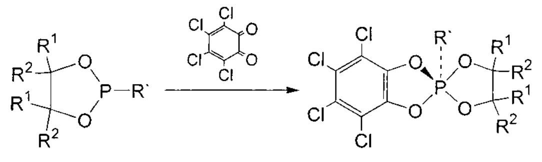
442 441

Also, the cyclic phosphite **443** reacts with phenanthrenequinone to form the phosphorane **444**.[317]



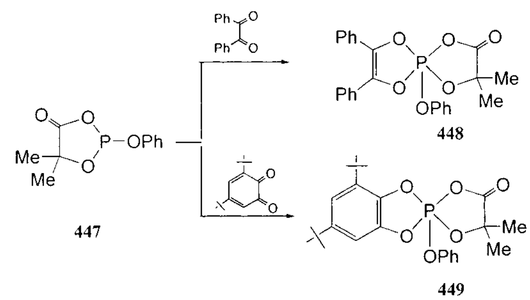
443 444

1,3,2-Dioxaphospholanes **445** (R^1 = H, R^2 = Me, R′ = Cl, NCS; R^1 = R^2 = Me, CF_3, R′ = Cl, OMe, NMe_2, OPh, SPh) react with *o*-chloranil in ether or boiling benzene to produce the corresponding spirophosphoranes **446**.[318−320]



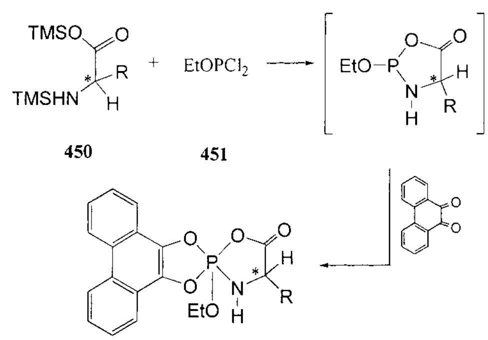
445 446

The reaction of benzil and 3,5-di-*tert*-butyl-*o*-benzoquinone with 4,4-dimethyl-2-phenoxy-1,3,2-dioxaphospholane-5-one (**447**) yields the relative pentaoxaphosphoranes **448** and **449**, respectively.[321]



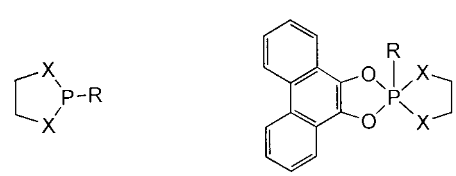
447

Also, acylaminotetraoxyspirophosphoranes (**452**, R = H, Me, *i*-Pr, *i*-Bu, CH_2Ph) are synthesized by the reaction of N,O-bis(trimethylsilyl) amino acid **450** with ethyldichlorophosphinite (**451**), which is followed by the addition of phenanthrenequinone in dry benzene under reduced pressure at 40 °C for 1 h. These acylaminophosphoranes **452** (R = Me, *i*-Pr, *i*-Bu, CH_2Ph) are found as pairs of diasterioisomers (NMR).[322]



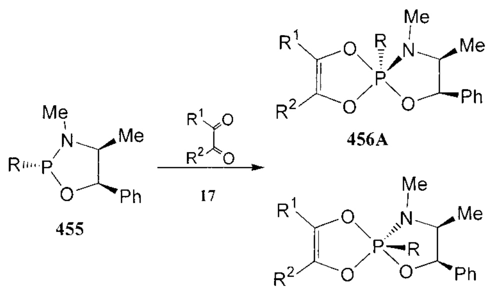
452

The condensation of tricoordinated phosphorus compounds **453** (X = O, S, NPh; R = Ph, Me, O-Xyl) with phenanthrenequinone leads to the formation of the phosphoranes **454**.[317,323] The structure of **454** (X = S, R = O-Xyl) was elucidated by X-ray crystallography.[323]



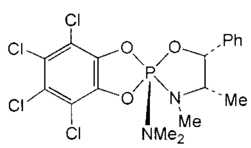
453 454

The chiral oxazaphospholidines **455** (R = Ph, *p*-$MeOC_6H_4$) react with α-diketones **17** ($R^1 = R^2$ = Me; $R^1 = R^2$ = Ph; R^1 = Me, R^2 = Ph) in dry pentane to form the corresponding spirophospholenes **456** as two diastereoisomers (A and B). The variable-temperature NMR studies of **456** show the stable configuration *trans*-**456A** below 60 °C, while above this temperature the *cis*-**456B** ratio is increased.[324]



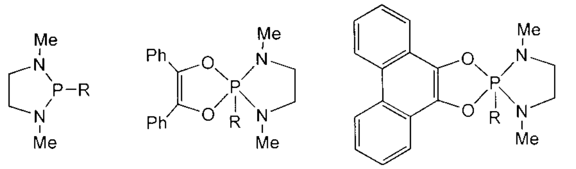
455 17 456A 456B

Reaction of *o*-chloranil with **455** (R = NMe_2) proceeds enantiospecifically to give spirophosphorane **457**, which was identified by X-ray analysis.[325]



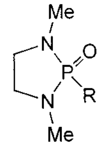
457

Cyclic aminophosphines **458** [R = OMe, NMe_2, $N(CH_2)_4$] react with benzil and phenanthrenequinone in dichloromethane at −70 °C to form the corresponding phosphoranes **459** and **460**, respectively.[276,277,326]



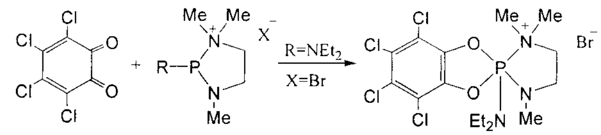
458 459 460

On the other hand, the reaction of acenaphthenequinone with cyclic aminophosphines **458** is quite vigorous in dichloromethane solution at −70 °C. When the solution is allowed to reach 20 °C, a deep brown mixture is produced from which the only isolable products are identified as the aminophosphine oxide derivatives **461**.[276]



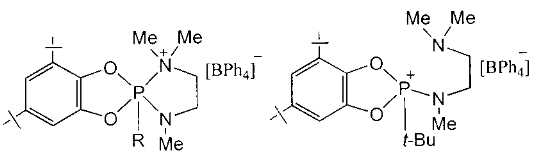
461

o-Chloranil reacts with 1,1,3-trimethyl-1,3,2-diazaphospholidin-1-ium salt (**462**, R = NEt_2, X = Br) in diethyl ether to yield the spirophosphorane **463** with an intact N→λ^5P donor−acceptor interaction.[327]



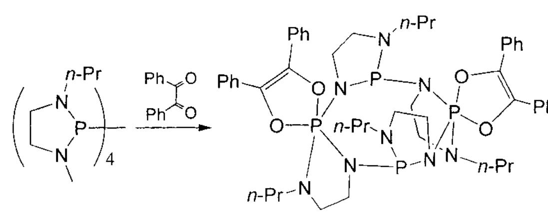
462 463

3,5-Di-*tert*-butyl-*o*-benzoquinone reacts with 1,3,2-diazaphospholidin-1-ium salts (**460**, R = Me, Ph, NEt_2; X = BPh_4) in dichloromethane solution to produce the corresponding phosphoranes **464**, whereas its reaction with **462** (R = *t*-Bu, X = BPh_4) yields the phosphonium salt **465**, which exhibited no significant N→λ^5P donor−acceptor interaction.[327]



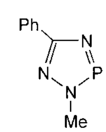
464 465

λ^3-Phosphazene oligomers **466** with benzil in xylene at 140 °C leads to the formation of the product **467**.[328]

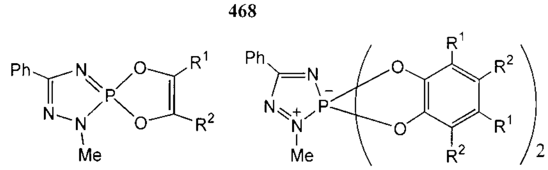


466 467

Reaction of biacetyl (**17**, $R^1 = R^2$ = Me) and benzil (**17**, $R^1 = R^2$ = Ph) with triazophosphole **468** gives the spirocyclic phosphorus compounds **469** by a 1:1 addition at the phosphorus atom,[328] while *o*-chloranil and 3,5-di-*tert*-butyl-*o*-benzoquinone react with **468** to form the hexacoordinated products **470** ($R^1 = R^2$ = Cl; R^1 = *t*-Bu, R^2 = H).[328]



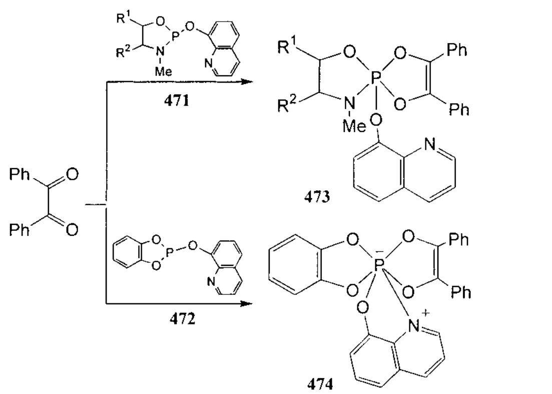
468



469 470

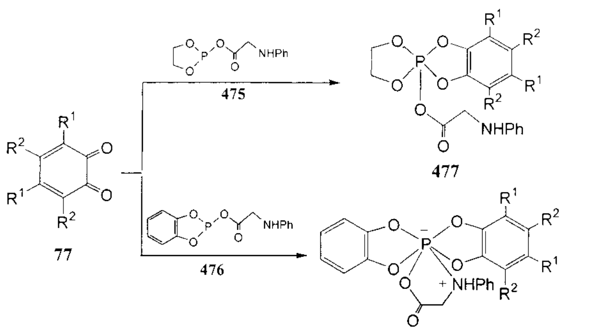
Cong and co-workers[329] isolated a number of hexacoordinated phosphorus compounds, all of a similar kind, which in some cases are found to equilibrate with pentacoordinate forms. The reaction of trivalent cyclic phosphorus compounds **471** ($R^1 = R^2$ = H; R^1 = Me, R^2 = Ph) and **472** with benzil in dichloromethane at 35 °C gives the corresponding pentacoordinated adducts **473** and hexacoordinated form **474**, respectively.[329]

Phenanthrenequinone [**77**, $R^1R^2 = (CH)_4$] and 3,5-di-*tert*-butyl-*o*-benzoquinone (**77**, R^1 = *t*-Bu, R^2 = H)



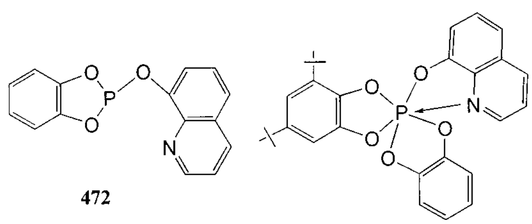
471 472 473 474

react with cyclic phosphites **475** and **476** to give the products **477** and **478**, respectively.[329]



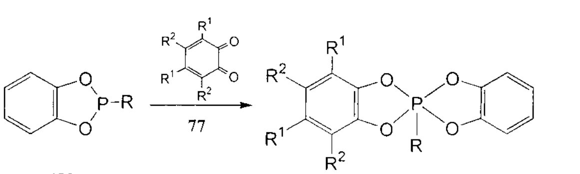
77 475 476 477 478

The tricyclic hexacoordinated phosphorane **479** is formed from the reaction of cyclic phosphite **472** with 3,5-di-*tert*-butyl-*o*-benzoquinone in boiling toluene and was confirmed by X-ray analysis.[330]



472 479

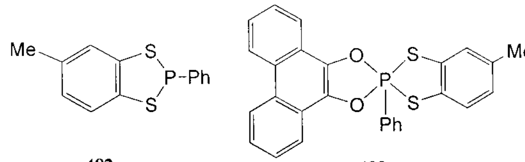
The reaction of phosphole derivatives **480** (R = Me, Ph, Cl, NHPh, $NMeCH_2CH_2NMe_2$) with *o*-quinones **77** ($R^1 = R^2 =$ H, Cl; $R^1 = t$-Bu, $R^2 =$ H) affords the 2,2′-spirobi(1,3,2-benzodioxaphospholes) **481**.[331−334]



480 481

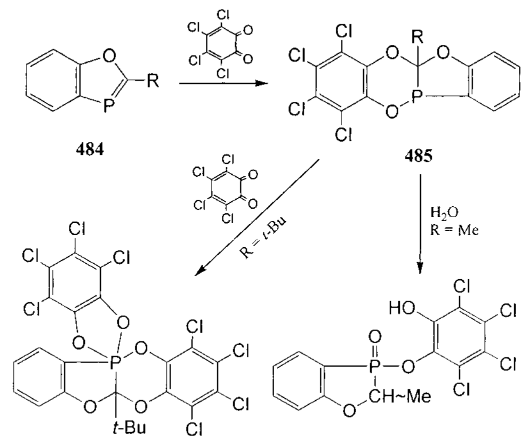
Similarly, the phosphorane **483** is produced from reaction of phenanthrenequinone with phosphorus reagent **482**.[335]

The 1,3-benzoxaphospholes **484** (R = Me, *t*-Bu) react likewise with *o*-chloranil to form [4 + 2]-cycloadducts **485**,[336] which with more *o*-chloranil undergoes a 1,1-addition at the phosphorus atom to give **486**.[336] The bicyclic phosphorus compound **485** (R = Me) upon hydrolysis yields the phosphinic acid aryl



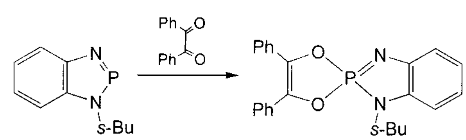
482 483

ester **487**. The structure of **485** (R = Me) has been confirmed by X-ray analysis.[337]



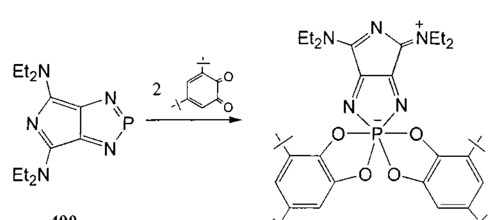
484 485 486 487

Reaction of 1,3,2-benzodiazaphosphole (**488**) with benzil in xylene at 140 °C forms the spirocyclic product **489**.[328]

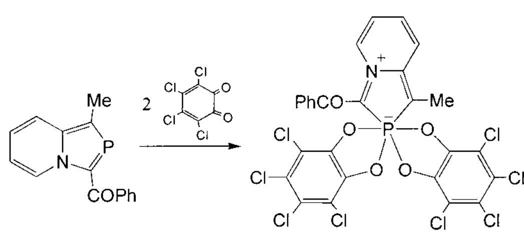


488 489

Electron-rich heterophospholes such as 4,6-bis-(diethylamine)-1,3,5-triaza-2-phosphapentalene (**490**) and 2-phosphaindolizine (**492**) add to 3,5-di-*tert*-butyl-*o*-benzoquinone and *o*-chloranil to yield the corresponding zwitterionic compounds **491** (as three isomers) and **493**, respectively.[338] The hexacoordinated 1:2-adducts **491** and **493** show a characteristic upfield ^{31}P NMR shift.[338]

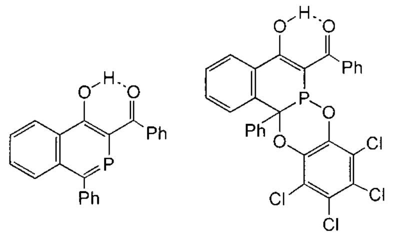


490 491



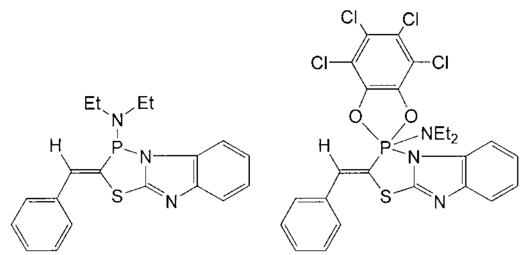
492 493

The isophosphinoline **494** reacts with *o*-choranil in toluene at −78 °C to form a light yellow solid of the polycyclic compound **495**.[339]



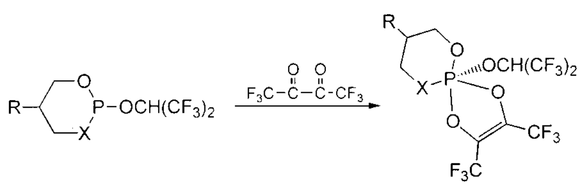
494 495

[1,3,4]Thiazaphospholidine **496** reacts with *o*-chloranil in dichloromethane to give the spirocyclic compound **497** as the (*Z*)-isomer.[340]



496 497

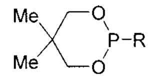
The cyclic phosphites **498** (R = Ph, *t*-Bu, H; X = O, NMe) react with hexafluorobiacetyl to yield the corresponding pentacovalent phosphorus compounds **499**.[341−343]



498 499

Oxidative addition reaction of cyclic phosphite **500** (R = Cl) with benzil at 130 °C for 24 h and with phenanthrenequinone at 170 °C for 48 h affords the phospholene structures **501** and **502**, respectively,[331] while the cyclic phosphites **500** (R = NEt_2, NHC_6H_{11}, Ph, OPh, O-Xyl, S-Xyl) with benzil and *o*-quinones produce the spirocyclic oxyphosphoranes **503** and **504** [$R^1 = R^2$ = Cl; R^1 = *t*-Bu, R^2 = H; $R^1R^2 = (CH)_4$], respectively.[330,332,344−347] The X-ray crystallography of **504** [R = Ph, S-Xyl, O-Xyl, NEt_2; $R^1R^2 = (CH)_4$] was determined.[330,346,347] The molecular geometry about the phosphorus atom for all cyclic phosphoranes **504** can be referred to a trigonal bipyramid.

Phenanthrenequinone reacts with cyclic phosphites **505** (X = S, NMe) and **506** in the absence of solvent to yield the bicyclic products **507** and **508**, respec-



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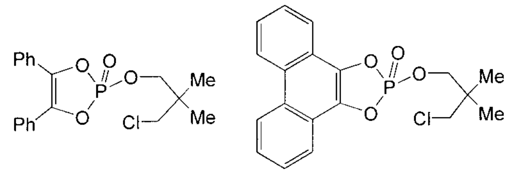
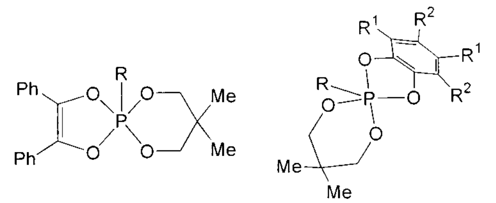
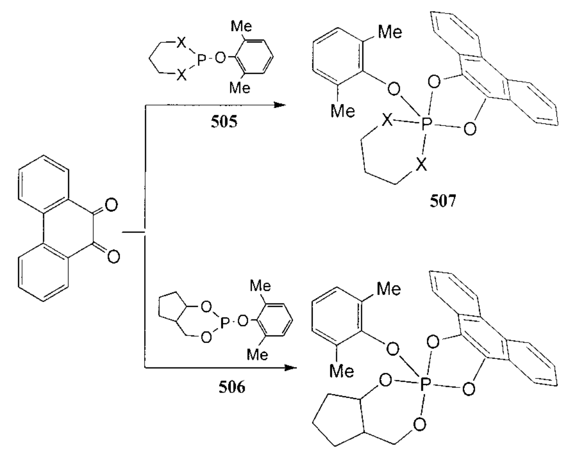


501 502



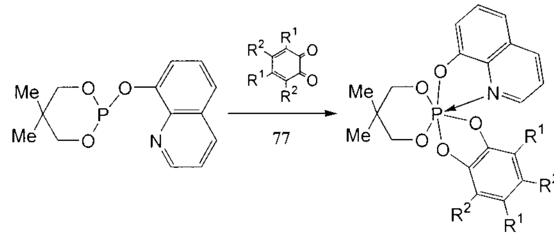
503 504

tively. They have a triagonal bipyramid structure, as identified by X-ray crystallography.[346,348]



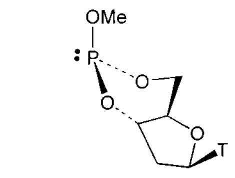
505 506 507 508

The oxidative addition of phenanthrenequinone **77** [$R^1R^2 = (CH)_4$] and 3,5-di-*tert*-butyl-*o*-benzoquinone **77** (R^1 = *t*-Bu, R^2 = H) to the cyclic phosphite **509** in boiling toluene or *p*-xylene for 10 min affords the tricyclic hexacoordinated phosphoranes **510** with internal N→P coordination, which was characterized by X-ray analysis.[330]



509 510

cis-Thymidine 3′,5′-cyclic methyl phosphite (**511**) and *cis*-thymidine 3′,5′-cyclic 2-methoxyethyl phosphite (**513**) react with 1 equiv of tetrachloro-1,2-benzoquinone at −80 °C in dichloromethane to give the nucleoside cyclic 3′,5′ P^v-trigonal bipyramidal (TBP) phosphorus compounds **512** and **514**.[349] These products were studied as the model for the enzymatic and nonenzymatic reactions involving cyclic adenosine 3′,5′-monophosphite (cAMP). The compound features equatorial−axial orientation of the 3′,5′-dioxaphosphorinane ring. The design of **514**, which incorporates OCH_2CH_2OMe as a conformational probe, shows from its ^1H NMR analysis the conformational transmission in the probe fragment, which indicates that the molecular structure with diequatorial orientation of the 3′,5′-ring and axial location of OCH_2-CH_2OMe contribute significantly to the pseudorotational equilibrium.[349]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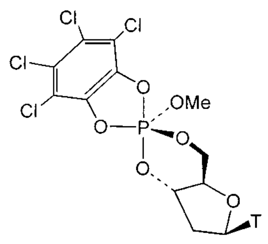
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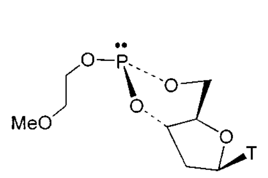
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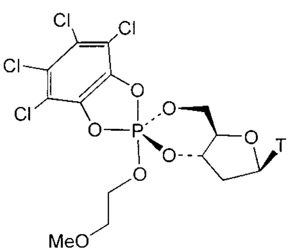
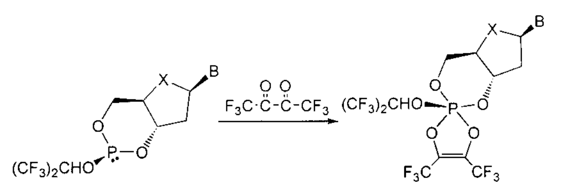
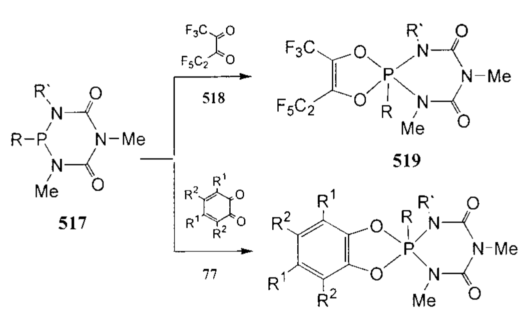
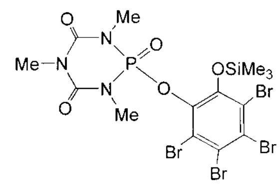

514

The cyclic phosphites **515** (X = O, CH_2; B = thymin-1-yl, H) react with hexafluorobiacetyl at low temperature to form the corresponding phosphoranes **516**,[341] which are designed as models for cAMP-enzyme or cAMP−H_2O (or transition states) in biological systems.

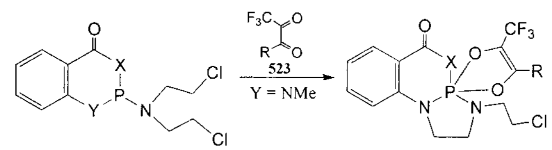

515 516

1,3,5,2-Triazaphosphorinanediones [**517**, R = $NHCH_2CH_2Cl$, $N(CH_2CH_2Cl)_2$; R′ = Me] react with perfluorinated diketone **518** in dichloromethane at room temperature to furnish the spirophosphorane derivatives **519**.[350] Similarly, the triazaphosphinanediones **517** [R = NMe_2, R′ = Me, Ph; R = NEt_2, NPh_2, F, R′ = Me; R = $N(C_6H_{11})_2$, R′ = Me] with *o*-quinones **77** (R^1 = R^2 = Cl, Br; R^1 = *t*-Bu, R^2 = H) in dichloromethane led to the respective oxidation products of spirophosphoranes **520**.[351] On the other hand, tetrabromo-*o*-benzoquinone reacts with **517** (R = $OSiMe_3$, R′ = Me) in dichloromethane at 0 °C to yield the phosphoryl compound **521**.[352]

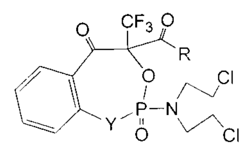

517 519 520

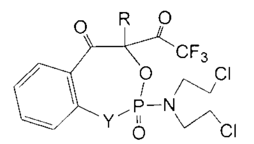

521

The reaction of benzodiazaphosphorinones **522** (X = $NCH_2C_6H_4F$-*p*, $NCH_2C_6H_4Cl$-*p*, $NCH_2C_6H_4Cl$-*o*; Y = NMe) with perfluorinated α-diketones **523** (R = C_2F_5, C_3F_7) in dichloromethane is accompanied by an unusual N-alkylation reaction, involving one of the two $ClCH_2CH_2$ groups bonded via nitrogen to the phosphorus atom. The alkylation reaction leads to ring closure and formation of the tricyclic phosphorane ring systems **524**.[353,354] While, benzoxaza- and

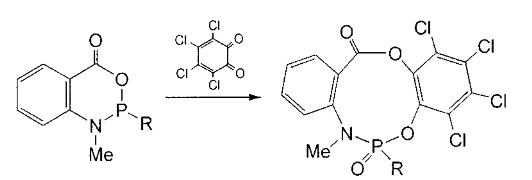

522 524

benzodioxaphosphorinone derivatives **522** (X = O, Y = NMe; X = Y = O) react with the perfluorinated α-diketones **523** [R = $CF(CF_3)_2$, $(CF_2)_2CF_3$] in dichloromethane with insertion of the diketones into the heterocycle of **522** with formation of compounds **525** (Y = O, NMe) as two isomers, **525A** and **525B**.[350]

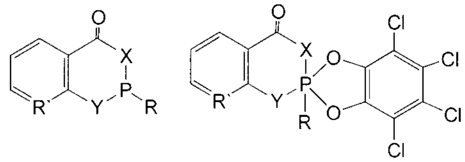

525A


525B

The reaction of the diethylamino- and bis(2-chloroethyl)amino-1,3,2-oxazaphosphorinone derivatives **526** [R = NEt_2, $N(CH_2CH_2Cl)_2$] with *o*-chloranil does not lead to the expected spirocyclic products by oxidative addition of the quinone to the λ^3P-atom. Instead, cleavage and expansion of the heterocyclic ring system with formation of the tricyclic products **527** are found to occur.[354−356] The structure of these products was confirmed by single-crystal X-ray structure determination.[355,356]

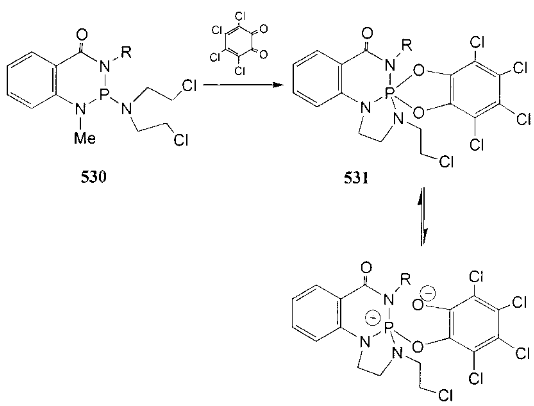

526 527

The oxidative addition of *o*-chloranil at the phosphorus atom of phosphorinanone derivatives **528** [X = O, NMe, Y = NMe, R = CN, R′ = CH; X = Y = NMe, R = NMe_2, R′ = N; X = Y = O, R = OMe, OEt, OCH_2CF_3, $OCH_2CF_2CHF_2$, $OCH_2(CF_2)_4H$, OC_6F_5, NEt_2, R′ = CH; X = Y = NMe_2, R = NMe_2, R′ = CH] produces the spirophosphoranes **529**.[356−360]



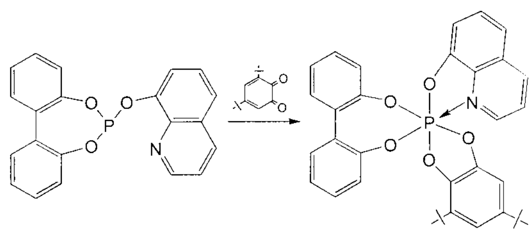
528 **529**

On the other hand, the diazaphosphorinones **530** (R = $CH_2C_6H_5$, $CH_2C_6H_4Cl$-*o*,$CH_2C_6H_4F$-*p*) are oxidized with *o*-chloranil in toluene to form the tricyclic phosphoranes **531**.[361,362] The ^{31}P NMR spectra of solutions of **531** recorded at room temperature within 1 h of their preparation revealed two signals, one in the range $\delta = -35.57$, typical of λ^5P, as in **531**, and the other in the range $\delta = 7.20-7.40$, which indicates an equilibrium between the phosphoranes **531** and their zwitterionic isomers **532**.[362]



530 **531** **532**

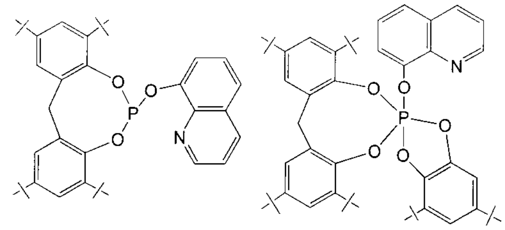
3,5-Di-*tert*-butyl-*o*-benzoquinone reacts with the cyclic phosphite **533** in boiling toluene to give the tricyclic hexacoordinated phosphorane **534** with an N→P bond, and the coordinating nitrogen is trans to an oxygen of the seven-membered ring (X-ray).[330]



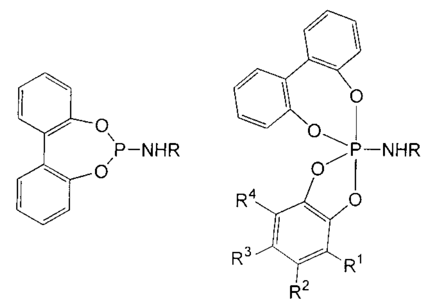
533 **534**

Also, the same *o*-quinone reacts with cyclic phosphite **535** under the same experimental condition to yield the pentacoordinated phosphorane **536** without an N→P bond, and the eight-membered ring spans a diequatorial position in a trigonal bipyramidal arrangement.[330]

The cyclic aminophosphite **537** (R = Me, C_6H_{11}) reacts with *o*-chloranil, 3,5-di-*tert*-butyl-*o*-benzoquinone, and phenanthrenequinone to afford the corresponding aminophosphoranes **538** [R = Me, C_6H_{11}, $R^1 = R^2 = R^3 = R^4$ = Cl; R = Me, $R^1 = R^3$ = *t*-Bu, $R^2 = R^4$ = H; R = C_6H_{11}, $R^1R^2 = R^3R^4 = (CH)_4$], in which the seven-membered ring tends to prefer the axial−equatorial (a−e) position in a trigonal bipyramidal geometry (X-ray).[332,363]

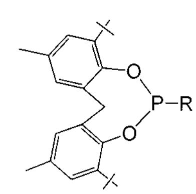


535 **536**



537 **538**

The relative apicophilicities of several substituents in spirophosphoranes **540**[332,364] produced from reaction of cyclic phosphorus reagents **539** (R = Me, Ph, NHMe, NMe_2, NHC_6H_{11}, N_3, SC_6H_4Cl-p) with *o*-chloranil depend on electronegativity, π-interactions (with phosphorus), and steric factors.[365,366] The X-ray crystallography studies reveal that the spirophosphoranes **540** have the isomeric trigonal bipyramidal structures **540A** and **540B**. In the case of R = Ph, NMe_2, N_3, SC_6H_4Cl-*p*, the eight-membered ring is situated in diequatorial (e−e) sites and the more apicophilic group R is located at an axial position to give structure **540A**, while in case of R = Me, NHMe, NHC_6H_{11}, the eight-membered ring is axial−equatorial (a−e) and the group R is in the equatorial position to form structure **540B**.[332,364]



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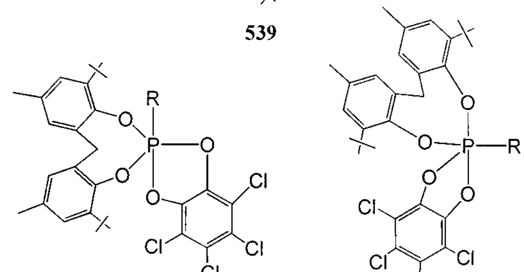
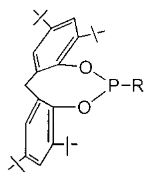


540A **540B**

The oxidative addition reaction of the appropriate cyclic phosphine **541** (R = Ph) and cyclic phosphite **541** (R = OCH_2CF_3) to benzil under nitrogen atmosphere at 180 °C for 1 h yields the new bicyclic phosphoranes **542** (R = OCH_2CF_3, Ph). Also, *o*-chloranil and 3,5-di-*tert*-butyl-*o*-benzoquinone react with **541** to form the phosphoranes **543** (R = Et, Ph, OCH_2CF_3, $R^1 = R^2$ = Cl; R = OCH_2CF_3, R^1 = *t*-Bu, R^2 = H).[367−369] Thus, X-ray analysis of **543** (R = Et,



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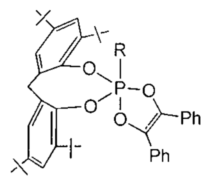

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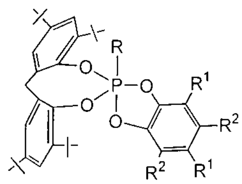
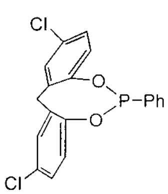


543

Ph, $R^1 = R^2$ = Cl) showed the least electronegative ligands, ethyl and phenyl groups, occupying the axial position of a trigonal bipyramid.[368,369] The reaction of *o*-chloranil with [2,2′-methylenebis{(4-chlorophenyl)-oxy}]phenylphosphine (**544**) in boiling toluene for 1 h gives the phosphorane **545**, which was characterized by X-ray analysis to reveal a trigonal bipyramidal geometry with electron-withdrawing chlorine substituents on each ring assuming the more conventional geometry with the rings occupying axial−equatorial positions and the phenyl group located in the remaining equatorial site.[368]



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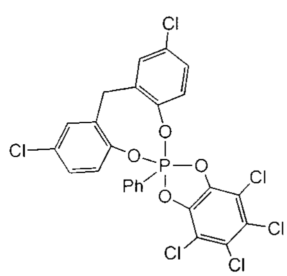
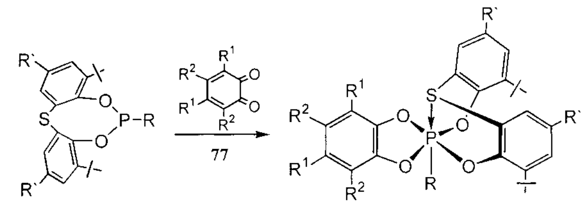


545

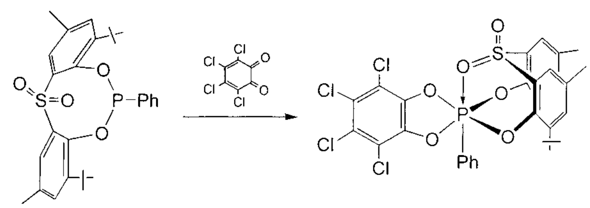
o-Chloranil **77** ($R^1 = R^2$ = Cl) and phenanthrenequinone **77** [$R^1R^2 = (CH)_4$] react with cyclic phosphites **546** (R = OCH_2CF_3, R′ = *t*-Bu; R = OC_6F_5, R′ = Me) and appropriate cyclic phosphines **546** (R = Ph, R′ = *t*-Bu; R = Cl, NHC_6H_4Me-*p*, NMe_2, $NHCH_2Ph$, R′ = Me) to produce the sulfur-donor-coordinated phosphoranes **547** [$R^1 = R^2$ = Cl, R = Cl, NMe_2, NHC_6H_4Me-*p*, OC_6F_5, R′ = Me; $R^1 = R^2$ = Cl, R = Ph, OCH_2CF_3, R′= *t*-Bu; $R^1R^2 = (CH)_4$, R = Cl, NMe_2, $NHCH_2Ph$, OC_6F_5, R′ = Me]. The structure of **547** was confirmed by X-ray analysis.[370−372]

The cyclic tetraoxyphosphorane **549** is prepared by oxidative addition reaction of [sulfurylbis{2-(4-methyl-6-*tert*-butylphenoxy)}]phenylphosphine (**548**) to *o*-chloranil in boiling toluene.[373] The ^{31}P and ^{1}H NMR data indicate the presence of two isomeric forms for



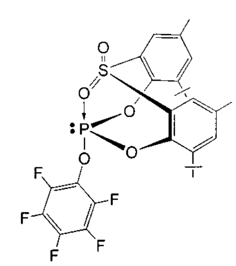
546 **547**

the phosphorane **549**, and X-ray study shows hexacoordinated phosphorus with octahedral geometry as a result of donor action from one of the oxygen atom of the sulfonyl group.[374]



548 **549**

By the same manner, the bicyclic phosphite **550** reacts with *o*-chloranil to form only one isomer from cyclic pentaoxyphosphorane **551**, which has an octahedral geometry (X-ray).[375]



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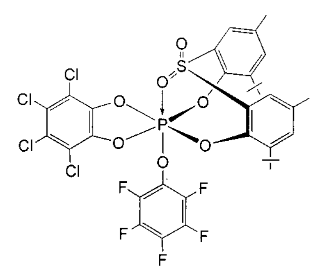
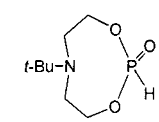


551

The reaction of 6-*tert*-butyl-1,3,6,2-dioxazaphosphocane 2-oxide **552** with *o*-chloranil in benzene at 20 °C affords the product which in solution gives an equilibrium mixture of a hexacoordinated phosphorus compound with a P−OH bond (**553**) and the phosphate ester **554** in the ratio 2:3 (^{31}P NMR).[376] A



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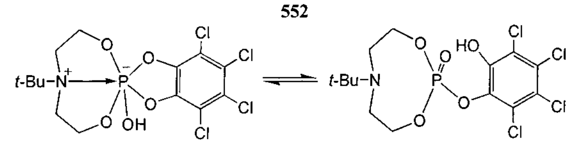
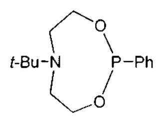


553 **554**

transannular phosphorus−nitrogen interaction is assumed to occur in structure **553**. While, 2-phenyl-6-*tert*-butyl-1,3,6,2-dioxazaphosphocane (**555**) with *o*-chloranil in benzene solution at room temperature produces a tautomeric equilibrium mixture of the tetra- and hexacoordinate phosphorus compounds

556 and **557** in ratio 3:2, which was detected by ^{31}P NMR.[376]



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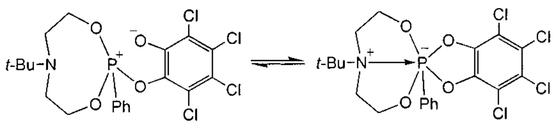
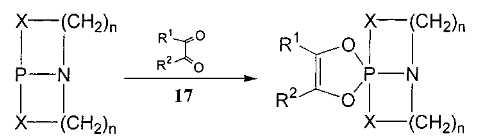


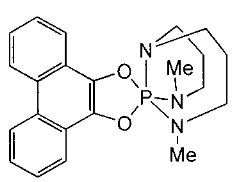
556 557

Biacetyl (**17**, $R^1 = R^2 =$ Me) and benzil (**17**, $R^1 = R^2 =$ Ph) react with bicyclic phosphorus compounds **558** (X = O, NMe; $n = 2, 3$) under nitrogen or argon atmosphere to produce the corresponding oxazaphosphoranes **559**.[377−379]



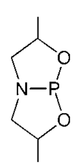
558 559

Similarly, phenanthrenequinone reacts with 2,8-dimethyl-2,5,8-triaza-1-phosphabicyclo[3.3.0]octane (**558**; X = NMe, $n = 3$) in deuterated chloroform at −10 °C to form the aminooxyphosphorane **560**.[379]



560

o-Chloranil reacts with the diastereoisomeric bicyclic phosphanes **561** in benzene at room temperature to give the two isomers **562A** and **562B** in ratio 7:3 (^{31}P NMR).[380]



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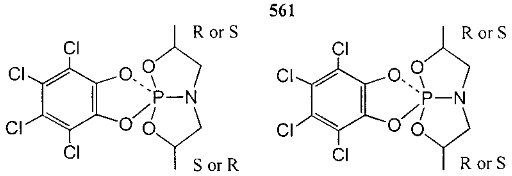
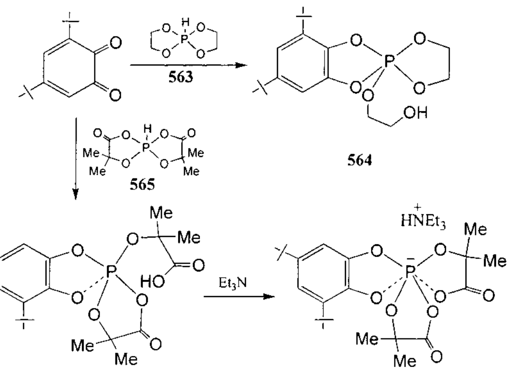


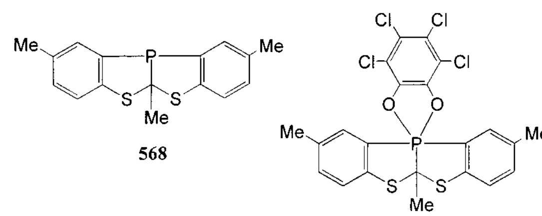
562A 562B

3,5-Di-*tert*-butyl-*o*-benzoquinone reacts with the spirophosphorane **563** in dichloromethane solution to form the spirophosphorane **564**.[381] Also, it reacts with the phosphorane **565** in tetrahydrofuran to produce the γ-hydroxyphosphorane **566**, which upon treatment with triethylamine affords the hexacoordinated phosphorus compound **567**.[382]



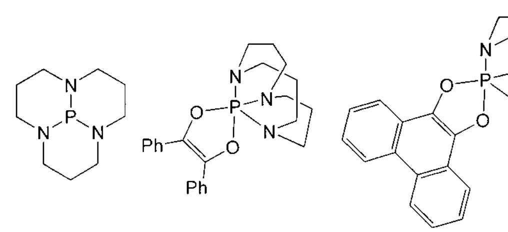
566 567

The reaction of fused 1,3-benzothiaphosphole **568** with *o*-chloranil yields the spiro pentacoordinated phosphorus adduct **569**.[383] The X-ray structural analysis of spiro compound **569** shows a trigonal bipyramidal configuration at phosphorus in which the three rings assume axial−equatorial positions.[383]



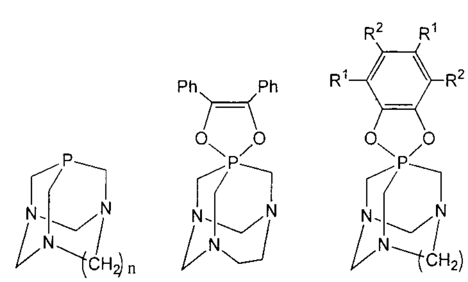
569

Condensation reaction of the macrocyclic phosphine **570** with benzil in deuterated dichloromethane at room temperature gives the phosphorane **571** on the basis of ^{31}P NMR chemical shift.[379] Also, it reacts with phenanthrenequinone in deuterated benzene at −10 °C under nitrogen atmosphere to form the aminooxyphosphorane **572**.[379]



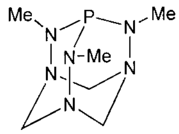
570 571 572

Phosphor(III)adamantane **573** ($n = 2$) reacts with benzil to give the spirophosphorane **574**. Similarly, 9,10-phenanthrenequinone or 3,5-di-*tert*-butyl-*o*-benzoquinone reacts with phosphor(III)adamantanes **573** ($n = 0, 1, 2, 6$) to produce the corresponding phosphoranes **575**.[384,385]

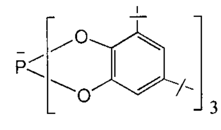


573 574 575

On the other hand, treating 3,5-di-*tert*-butyl-*o*-benzoquinone with phosphor(III)adamantane **576** gives the hexacoordinated product **577**.[385]

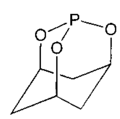


576



577

Hexafluorobiacetyl reacts very rapidly with 1-phospha-2,8,9-trioxaadamantane (**578**) to give the caged polycyclic pentaoxyphosphorane **579**.[201] From its ^{1}H, ^{19}F, and ^{31}P NMR studies, the oxyphosphorane is formulated as trigonal bipyramids with the five-membered ring in an apico–equatorial skeletal position and with the ligands undergoing a relatively rapid exchange among the skeletal positions by the intramolecular mechanism termed the "turnstile rotation".[201,386−389] Also, the spirophosphoranes **580** [R^1 = *t*-Bu, R^2 = H; R^1R^2 = $(CH)_4$] are formed from the reaction of phosphore(III)adamantane **578** with 3,5-di-*tert*-butyl-*o*-benzoquinone and 9,10-phenanthrenequinone.[384]



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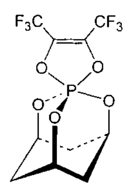

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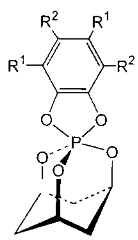
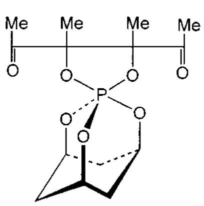


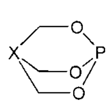
580

The caged phosphites are quite unreactive toward biacetyl; however, the adamantenoid phosphite **578** reacts with biacetyl under suitable conditions and prolonged reaction times to form the diastereomeric 2:1 adducts **581** at a slow rate.[390]



581

Similarly, the phosphatrioxabicyclooctanes **582** (X = CMe, P) with biacetyl lead to the formation of mixtures of diastereomeric oxyphosphoranes **583**.[305,390]



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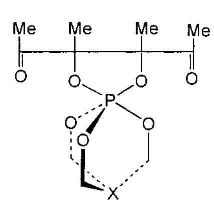
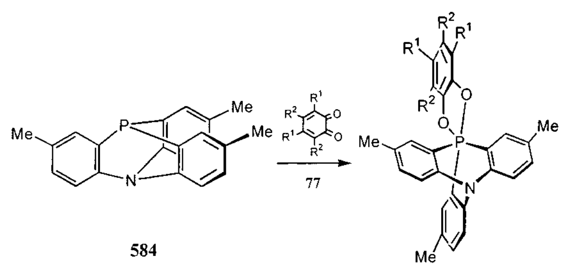


583

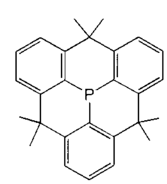
A possible explanation of these differences is that the reactions of the trivalent phosphorus compounds with carbonyl compounds may contain reversible and irreversible steps. The condensation of 1 mol of biacetyl with 1 mol of the phosphite probably contains several reversible steps leading eventually to the 1:1 oxyphosphorane. If this 1:1 adduct is of high energy as a result of ring strain and/or intramolecular crowding in the trigonal bipyramidal phosphorus compounds, it might not be observable. The carbon–carbon condensation step in the formation of the 2:1 adducts is probably essentially irreversible under most conditions; hence, there is an opportunity for isolation of the 2:1 phosphoranes.[390]

Cyclization of 2,8,15-trimethyl-5,10-[1,2]benzenophenophosphazine (**584**) with *o*-quinones **77** [R^1 = R^2 = Cl; R^1 = *t*-Bu, R^2 = H; R^1R^2 = $(CH)_4$] at about 170 °C in the absence of solvent yields the corresponding spirophosphoranes **585**, which, on account of the rigid tridentate ligand, offered favorable conditions for a novel ground-state geometry. However, an X-ray structural analysis of **585** (R^1 = R^2 = Cl) demonstrated the preeminence of a trigonal bipyramidal structural principle.[391]



584 585

Treating of cyclic phosphorus compound **586** with *o*-chloranil in benzene solution forms a trigonal bipyramidal phosphorane **587**, whose crystal structure is detected.[392]



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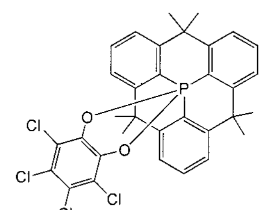
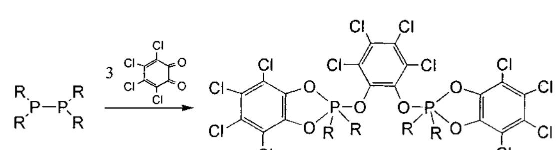


587

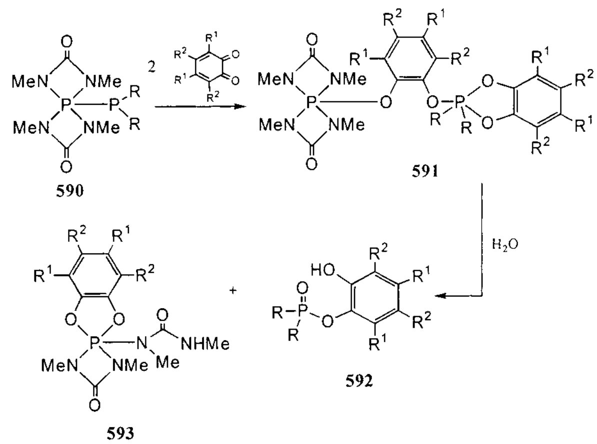
XIII. Reactions with Phosphorus Compounds Containing More Than One Phosphorus Atom

The symmetrical λ^3P–λ^3P diphosphorus compounds **588** (R = Me, Et, *t*-Bu, Ph, C_6H_{11}) react with *o*-chloranil in molar ratio 1:3 in ether or benzene solution to give the phosphoranes **589**,[393] which result from the oxidative addition of *o*-quinone to both λ^3P atoms and insertion of tetrachloro-*o*-catechol into the P–P bond.



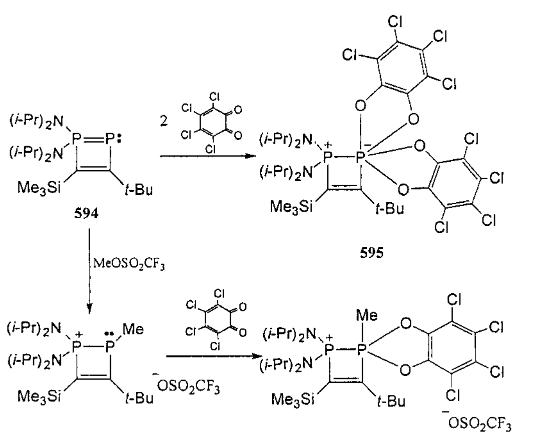
588 589

Reactions of unsymmetrical λ^5P$-\lambda^3$P diphosphorus compounds **590** (R = Me, Ph) with *o*-quinones **77** (R^1 = R^2 = Cl; R^1 = *t*-Bu, R^2 = H) lead not only to oxidative addition of the *o*-quinone to λ^3P but also to insertion of a further molecule of *o*-quinone to the P$-$P bond to form the phosphoranes **591**.[393] The hydrolysis of the products **591** with cleavage of a P$-$O$-$C (hydroquinone) bond and formation of mononuclear products **592** and **593** involves λ^4P and λ^5P, respectively. A mechanism of this hydrolysis is proposed and has been elucidated by independent synthesis of some products.[393]



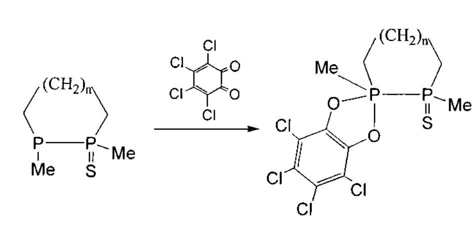
590 591 592 593

Addition of 2 equiv of tetrachloro-*o*-benzoquinone to 1σ^4,2σ^2-diphosphete **594** in ethereal solution at room temperature gives the 1σ^4,2σ^6-diphosphete **595** in 92% yield. Compound **594** reacts with 1 equiv of methyl trifluoromethanesulfonate to produce the cationic 1σ^4,2σ^3-diphosphete **596**, which reacts with 1 equiv of tetrachloro-*o*-benzoquinone in ethereal solution at room temperature to form the 1σ^4,2σ^5-diphosphete **597** in 86% yield.[394] The cyclic structure of **595** has been confirmed by a single-crystal X-ray diffraction study.[394]



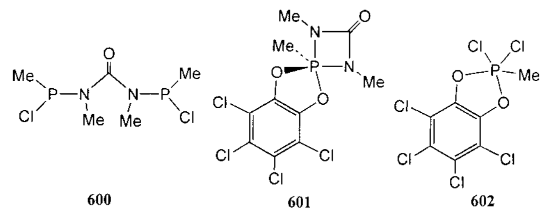
594 595 596 597

The cyclic diphosphane monosulfides **598** (*n* = 1,2) react with tetrachloro-*o*-benzoquinone by oxidative addition to afford oxyphosphoranes **599** with λ^4P$-\lambda^5$P bonds.[395]



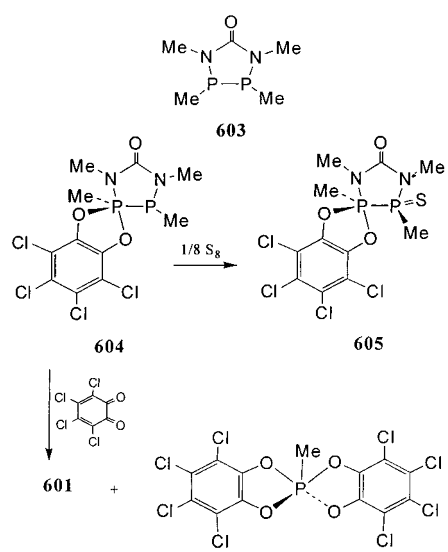
598 599

The chloro-substituted diphosphine **600** reacts with 2 mol of tetrachloro-*o*-benzoquinone in ethereal solution at 0 °C to furnish the spirophosphorane **601** with nonisolable dichlorophosphorane **602**.[396]



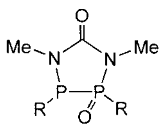
600 601 602

Dehalogenation of 2,6-dichloro-3,5-dimethyl-3,5-diaza-2,6-diphosphaheptan-4-one (**600**) with *n*-Bu_3P[397] or Me_3SnH[398] furnishes a good yield of diazadiphospholanone **603**, which reacts quantitatively with tetrachloro-*o*-benzoquinone to give the λ^5P$-\lambda^3$P diphosphorus compound **604**. A further oxidation of **604** with tetrachloro-*o*-benzoquinone at the λ^3P atom leads to cleavage of the P$-$P bond with formation of **601** and a further spirophosphorane **606**, which results from the oxidative addition of 2 equiv of tetrachloro-*o*-benzoquinone to a P$-$Me unit.[396,399] Addition of elemental sulfur to the λ^3 phosphorus atom in **604** furnishes the λ^5P$-\lambda^4$P diphosphorus compound **605**, whose structure has been determined by X-ray diffraction.[400]



603 604 605 601 606

Oxidation of the λ^3 phosphorus atom in diphosphorus compounds **607** (R = Et, $CHMe_2$) with *o*-chloranil gives the λ^5P$-\lambda^4$P adducts **608**, which were characterized by ^{1}H and ^{31}P NMR spectra and mass spectral fragmentation pattern.[401]



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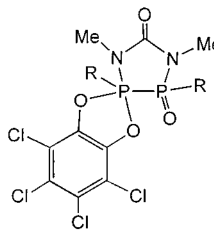
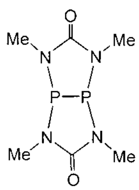


608

The oxidation of 2,4,6,8-tetramethyl-2,4,6,8-tetra-aza-1λ^3,5λ^3-diphosphabicyclo[3.3.0] octane-3,7-dione (**609**)[402] with *o*-chloranil in toluene at room temperature for 4 days affords the diphosphorane **610**



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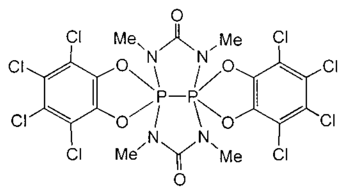
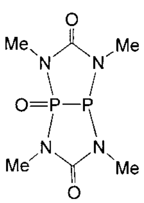


610

containing an axial λ^5P−λ^5P bond.[403] The molecular structure of **610** was confirmed by X-ray analysis, which shows that both phosphorus atoms display a basically trigonal bipyramidal geometry.[403] Also, the bicyclic compound with a λ^3P−λ^4P bond (**611**) reacts with *o*-chloranil to produce the spirocycle **612** with a λ^4P−λ^5P bond, which was characterized on the basis of ^{31}P NMR and mass spectra.[404]



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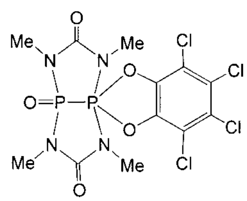
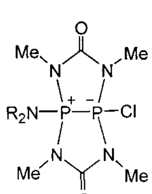


612

o-Chloranil reacts with diphosphorus compound **613**[405] containing a direct bond between the phosphonium and phosphoranide phosphorus atoms to form the phosphoniaphosphorate **614**, which is the first compound with a λ^4P−λ^6P bond.[405,406]



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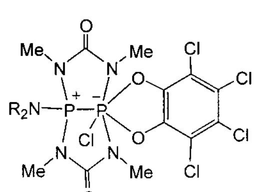
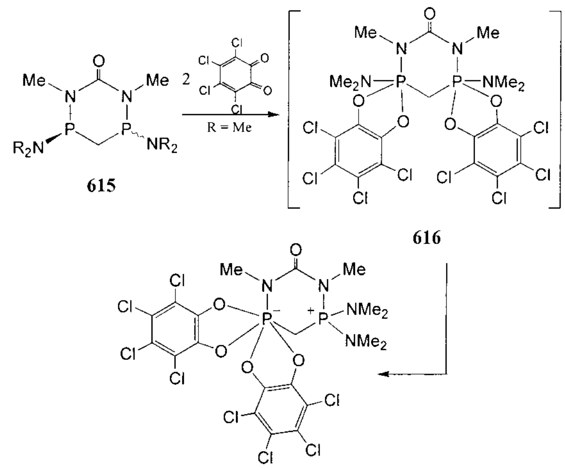


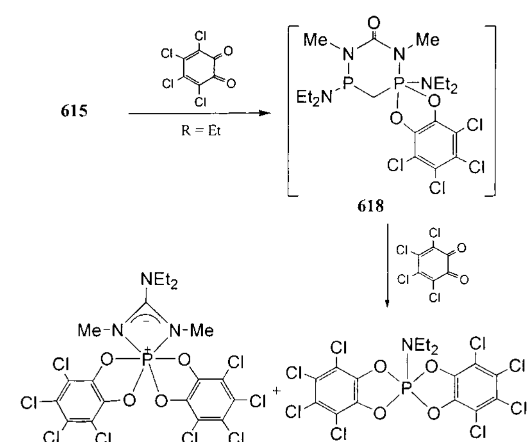
614

1,3-Diaza-4,6-diphosphorine (**615**, R = Me), consisting of a mixture of cis- and trans-isomers (1:9) is readily oxidized by 2 mol of *o*-chloranil in methylene chloride solution at room temperature to form unusual zwitterionic compound **617**, containing two phosphorus atoms of opposite charge and different coordination number through an intermediate phosphorane **616**.[407,408] The X-ray crystal structure analysis of **617** revealed the presence of a six-membered ring with an unusual conformation.



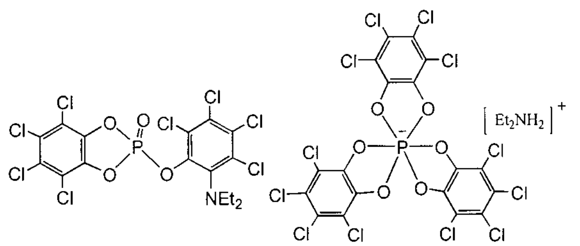
617

Compound **615** (R = Et), containing the bulkier diethylamino groups, reacts with *o*-chloranil in another way. The increase in steric hindrance at the phosphorus atoms changes the course of this reaction dramatically and leads to the cleavage of the original heterocycle.[409] The cleavage of heterocycle **615** (R = Et) is believed to be proceeded by the formation of an intermediate compound (**618**). Further addition of *o*-chloranil leads to the formation of a mixture of compounds including the 1,3,2-diazaphosphetidine **619** and the spirophosphorane **620**.[409] The spirophosphorane **620** is unstable and upon recrystallization or storage in methylene chloride solution is partially transformed into the phosphate **621**.[409] The mixture of the two isomers **620** and **621** rearranges slowly into the phosphonium salt **622**, containing a six-coordinate phosphorus atom. The structures of **619**, **620**, and **622** were established by low-temperature X-ray analysis.[409]



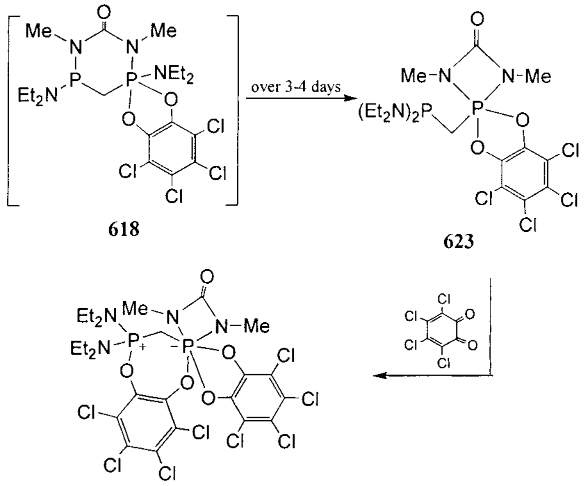
619 620

Also, the unstable phosphorane **618** previously obtained from the reaction of equimolar amounts of 1,3-diaza-4,6-diphosphorine (**615**, R = Et) and *o*-chloranil undergoes an unusual spontaneous rearrangement over 3−4 days into the isomeric methylenephosphinophosphorane **623**,[410] which is oxidized with *o*-chloranil at the two phosphorus atoms of **623** without cleavage to form the zwitterionic product



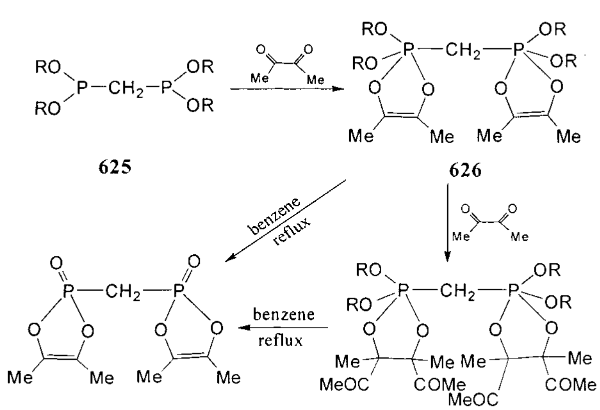
621 622

624, containing a seven-membered ring with two phosphorus atoms of opposite formal charge and different coordination number (λ^4P^+, λ^6P^-).[409] The mechanistic studies for the formation of the products **623** and **624** were discussed and the chemical properties have been investigated.[409,410]



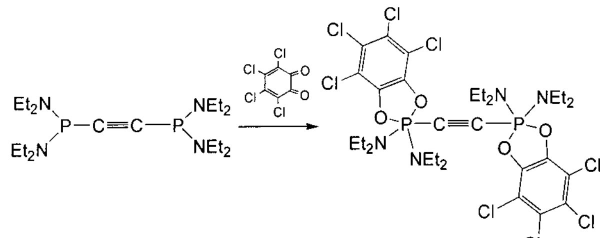
618 623 624

The reaction of tetraalkyl methylenebisphosphites **625** (R = Et, $CHMe_2$) with biacetyl gives the 1:2 adducts **626**. Further addition of biacetyl leads to the formation of bis(dioxaphospholane) **627**. The product **626** or **627** in refluxing benzene is decomposed to yield bis(dioxaphospholene) **628**.[411]



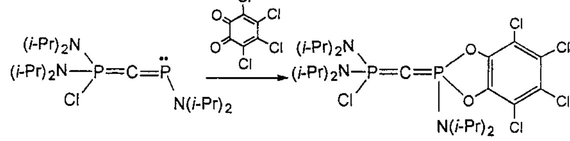
625 626 627 628

Similarly, diphosphorus-substituted acetylene **629** is oxidized at the two phosphorus atoms with *o*-chloranil in diethyl ether solution at −80 °C to form acetylenebis(tetrachlorobenzodiaminodioxaphospholane) **630** in 99.7% yield.[412]



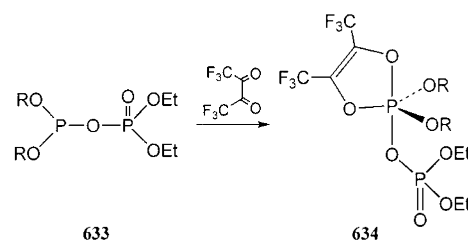
629 630

The lone pair of electrons at the phosphorus center in $1\sigma^4,3\sigma^2$-diphosphaallene **631** can be used for a formal [1 + 4]-cycloaddition with tetrachloro-*o*-benzoquinone to afford the carbodiphosphorane **632**, which is isolated in 62% yield.[413]



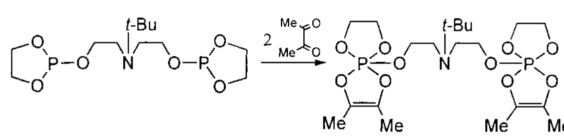
631 632

Hexafluorobiacetyl reacts with the substituted mixed anhydrides of phosphorus **633** (R = Me, Et), containing two phosphorus atoms of different coordinated number (λ^3P, λ^4P), in methylene chloride at −78 °C to form the oxyphosphorane anhydrides **634**[414] with $\lambda^5P{-}O{-}\lambda^4P$, which are assumed to have the trigonal bipyramidal geometry about λ^5P by analogy with other related oxyphosphoranes.[189,267,313,390,415] Compounds **634** are oxyphosphorane models of the hypothetical intermediates derived from the addition of nucleophiles to the phosphorus of the biochemically important pyrophosphates, such as adenosine 5′-diphosphate (ADP) and adenosine 5′-triphosphate (ATP).[414]



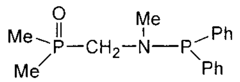
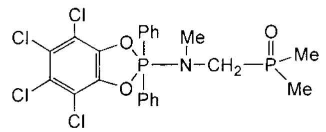
633 634

Biacetyl is condensed very readily with biphosphite **635** in benzene solution at 60 °C for 6 h to produce a nondistillable product whose ^{31}P NMR chemical shift (δ = −28.5 ppm) is consistent with other dispirophosphoranes and has the structure **636**.[416] On the



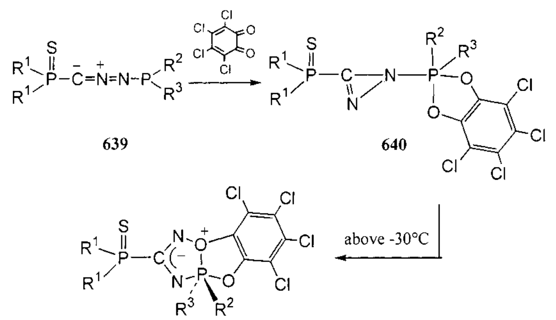
635 636

other hand, the oxidation of *N*-diphenylphosphino-*N*-methylaminomethylenedimethylphosphine oxide (**637**) by *o*-chloranil in deuterated dichloromethane at room temperature leads to the corresponding addition product **638**.[417]

637 638

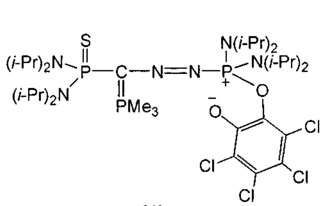
The reaction of the nitrilimine **639** [$R^1 = R^2 = R^3 = N(i\text{-}Pr)_2$] with *o*-chloranil in deuterated dichloromethane at −50 °C produces 1*H*-diazirine **640**,[418] which is rearranged above −30 °C to give the nitrene−oxygen complex **641**.[418,419] The addition of



639 640

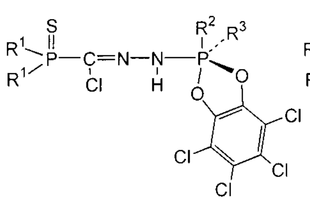
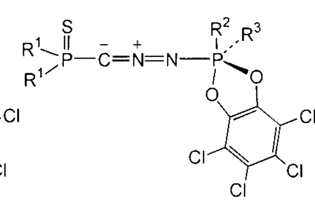
641

trimethylphosphine to **640** [$R^1 = R^2 = R^3 = N(i\text{-}Pr)_2$] in tetrahydrofuran at room temperature forms the phosphorus ylide **642**.[419]



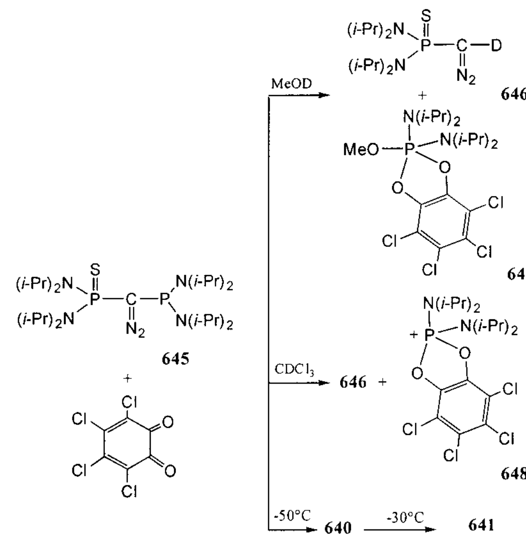
642

When a stoichiometric amount of *o*-chloranil is added to **639** [$R^1 = N(i\text{-}Pr)_2$, $R^2 = Ph$, $R^3 = 2,4,6\text{-}(CF_3)_3C_6H_2$] in tetrahydrofuran solution at −20 °C, a mixture of the three products **641**, **643**, and **644** is formed in 10:15:75 ratio.[420] The formation of hydrazonyl chloride **643** is in low yield, due to the presence of a small amount of HCl in the commercially available *o*-chloranil. An X-ray crystal structure determination was performed on **643** [$R^1 = N(i\text{-}Pr)_2$, $R^2 = Ph$, $R^3 = 2,4,6\text{-}(CF_3)_3C_6H_2$].[420]

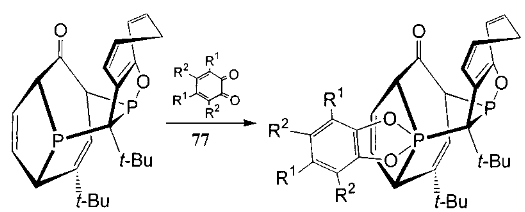



643 644

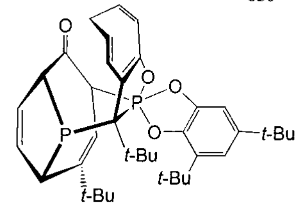
Also, *o*-chloranil reacts with the isomeric diazo derivative **645** in tetrahydofuran at −78 °C in the presence of a large excess of deuterated methanol to afford the C-deuterio diazo **646** and methoxyphosphorane **647**.[419] When the same reaction is carried out in the presence of deuterated chloroform, compounds **646** and phosphonium salt **648** are formed.[419] The bicyclic compound **641** [$R^1 = R^2 = R^3 = N(i\text{-}Pr)_2$] is produced from the reaction of diazo **645** with *o*-chloranil in dichloromethane solution at −30 °C via **640**.[419]



The pentacyclic cage phosphorus compound **649** reacts with *o*-quinones **77** ($R^1 = R^2 = Cl, Br$; $R^1 = t\text{-}Bu$, $R^2 = H$) in dichloromethane solution at room temperature to produce the spirocyclic adducts **650**, but when using 3,5-di-*tert*-butyl-*o*-benzoquinone **77** ($R^1 = t\text{-}Bu$, $R^2 = H$), an additional isomeric spirocyclic product (**651**) can be detected.[421]

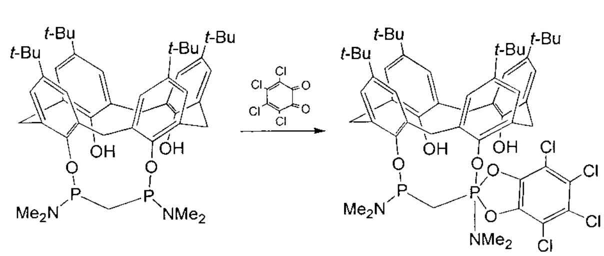


649 650



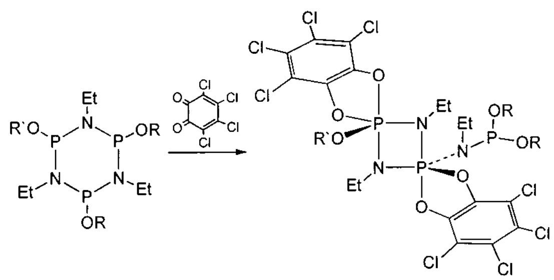
651

Calix[4]arene **652** can be oxidized easily with *o*-chloranil in toluene for 1 h at −20 °C to yield the monophosphorane **653**.[422]



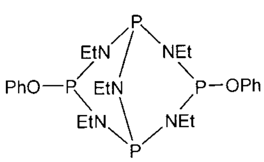
652 653

The λ^3-cyclotriphosphazanes **654** (R = R′ = 2,6-$Me_2C_6H_3$, 4-BrC_6H_4; R = 2,6-$Me_2C_6H_3$, R′ = 4-BrC_6H_4) possess three tricoordinated phosphorus centers that react with tetrachloro-*o*-benzoquinone in dichloromethane to yield the λ^5-cyclodiphosphazanes **655**[423,424] bearing an exocyclic aminophosphite moiety by an unusual ring contraction rearrangement, depending upon the nature of the substituents on the phopsphorus atoms.

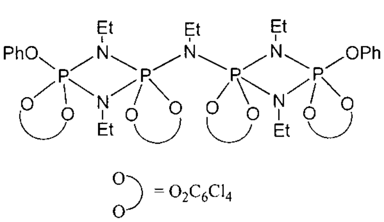


654 655

Also, the λ^3-bicyclic tetraphosphapentazane **656**, on treatment with tetrachloro-*o*-benzoquinone, undergoes a double ring contraction rearrangement to give the λ^5-cyclodiphosphazane **657**.[423] The molecular structure of **657** has been studied by X-ray analysis.

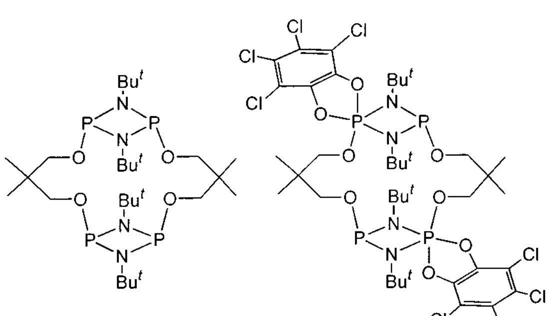


656



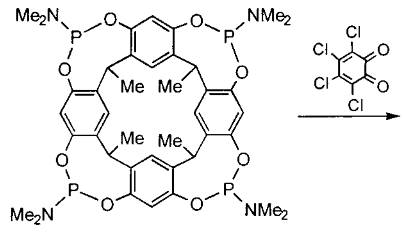
657

Recently, Kommana and Kumara Swamy reported[425] a new class of macrocycles based on a cyclodiphosphazane skeleton by the oxidation of compound **658** with tetrachloro-*o*-benzoquinone in dichloromethane solution at 25 °C for 2 days to form the macrocycle product **659**. The X-ray data of compound **659**·$3C_6H_5CH_3$, which is consistent with its solid-state structure, reveals the 16-membered macrocycle with two diol residues connecting the two cyclodiphosphazane units on each side.[425]



658 659

Compound **661**, involving four $\sigma^5\lambda^5$-phosphorus atoms, is prepared by oxidative addition of *o*-chloranil to **660**. The ^{31}P NMR spectrum of **661** shows groups of broad signals with four resonances.[426]



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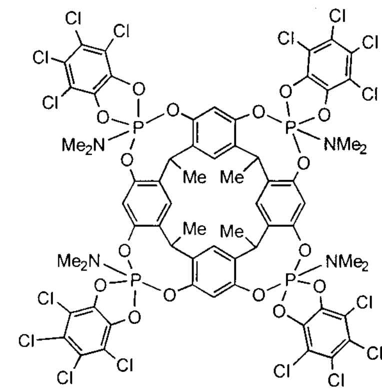
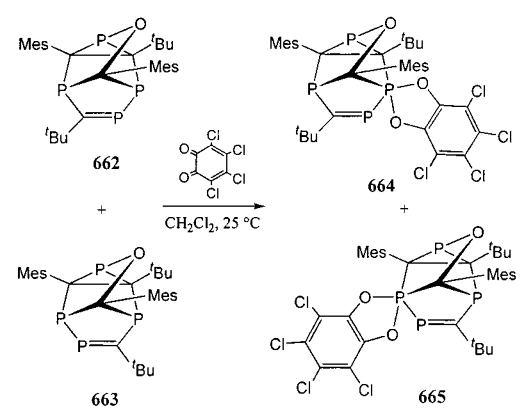


661

Tetrachloro-*o*-benzoquinone undergoes a selective [4 + 1]-cycloaddition with a mixture of the two regioisomers of oxatetraphosphadeltacyclenes **662** and **663** in methylene chloride at 25 °C for about 14 h, leading to spirocyclic products containing λ^5-phosphorus atoms (**664** and **665**, in ratio 9:1), isolated as a mixture in 69% yield by a chromatographic method.[427] The isomer **664** is obtained in the pure form by crystallization from pentane/ether/CH_2Cl_2 (3:1:1) at 0 °C, and its structure has been confirmed by X-ray crystallographic analysis.[427]

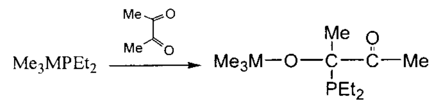


XIV. Reactions with Phosphorus–Metal Complexes

The compounds having a lone pair of electrons on the phosphorus atom give smaller or greater numbers of coordination compounds. Both inorganic and organic phosphorus compounds, simple and complex, bind to few or many transition metal and nontransition metal centers.[428] Ligands such as phosphines and amines are good σ donors in organometallic reactions and increase the electron density at the metal.[429]

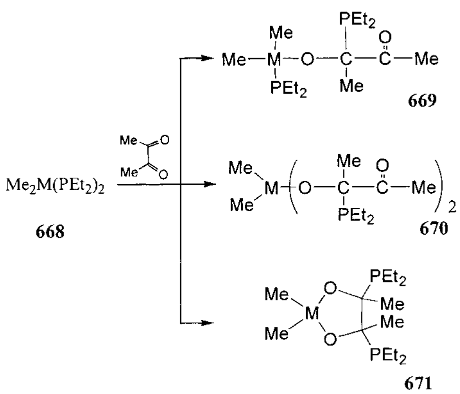
The metal complexes $Pt(PPh_3)_4$,[430−432] $Pd(PPh_3)_4$,[432] $M(NO)(PPh_3)_3$[433] (M = Co, Rh and Ir), $RhCl(PPh_3)_3$,[432] *trans*-MCl(CO)$(PPh_3)_2$ [432] (M = Rh and Ir), $Ru(CO)_3$-$(PPh_3)_2$,[434] and $RuCl_2(PPh_3)_3$ [434] have been shown to undergo both thermal and photoinduced oxidative addition or elimination reactions with certain *o*-quinones.

The germyl- and silylphosphines **666** (M = Ge, Si) are condensed by a dipolar 1,2-addition to one of the carbonyl groups of biacetyl and lead to the formation of phosphorus ketoalkoxygermanes or -silanes **667**.[435,436] While, the action of germyl- and silyl-

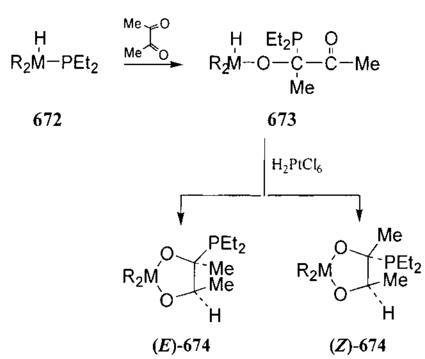


666 667

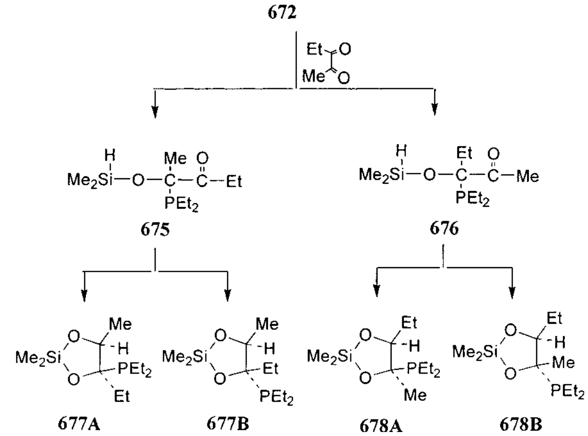
diphosphine **668** (M = Ge, Si) on biacetyl gives acyclic derivatives from 1,1- and 1,2-addition (**669**, **670**) and cycloaddition adduct **671** in 40:45:15 ratio, respectively.[435,436]



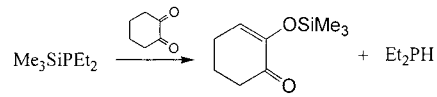
The condensation of the hydrometalphosphines **672** (M = Ge, R = Et; M = Si, R = Me) with biacetyl yields the product **673** with an M−H bond, which is cyclized by intramolecular addition in the presence of H_2PtCl_6 to give **674** as diasterioisomers (predominantly *E*-isomer).[435]



On the other hand, pentane-2,3-dione is added to diethyl(hydrodimethylsilyl)phosphine (**672**, R = Me, M = Si) at 70 °C to form the two isomers **675** (67%) and **676** (33%), which are cyclized at 100 °C in the presence of H_2PtCl_6 to form four stereoisomers, **677A,B** and **678A,B**.[435]

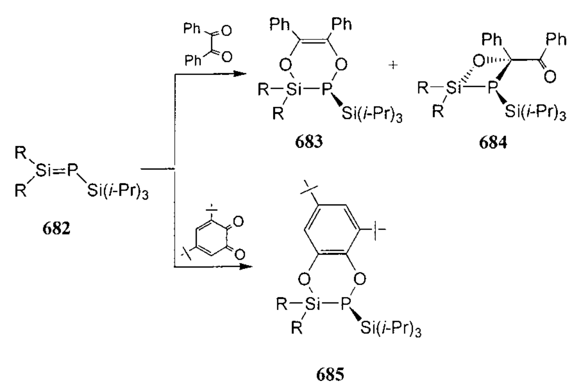


Cyclohexane-1,2-dione reacts with diethyl(trimethylsilyl)phosphine **679** at 40 °C to afford **680** along with diethylphosphine (**681**).[435]



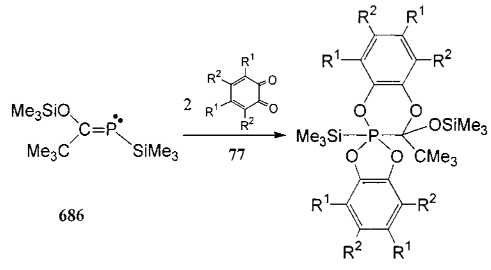
679 680 681

By treating silylidenephosphane **682** (R = 2,4,6-*i*-$Pr_3C_6H_2$) with benzil in toluene at 25 °C, surprisingly, the [2 + 4]-cycloadduct **683** is formed in 10% yield (^{31}P NMR) and the unexpected [2 + 2]-cycloadduct **684**, which has been isolated as the diasteriomerically pure form, is produced in 90% yield. When the above reaction mixture is heated at 110 °C for 3 h, compound **684** is the only product thus formed.[437] Also, 3,5-di-*tert*-butyl-*o*-benzoquinone with **682** in toluene at 25 °C furnishes the thermally resistant benzo-condensed heterocycle **685**. The ^{31}P chemical shift is identical with the value observed for **683** (116.3 ppm).[437]



The 1:2 reaction between the phosphaalkene **686** and the substituted *o*-quinones **77** ($R^1 = R^2$ = Cl, Br; R^1 = *t*-Bu, R^2 = H) proceeds via [4 + 2]-cycloadducts to give the phosphoranes **687**.[438]

The very reactive phosphorus−metal complexes **688** (M = Pd, *n* = 3; M = Pt, *n* = 3, 4) react with *o*-quinones **77** [$R^1 = R^2$ = Cl; $R^1R^2 = (CH)_4$] in dichloromethane solution to yield the diamagnetic complex **689**.[431,432] The molecular structure of **689** (R^1



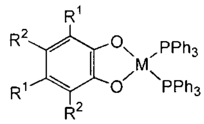
686

687

$= R^2 = Cl$, M = Pd) has been determined from X-ray analysis.[439]

M(PPh$_3$)$_n$

688

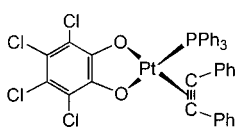


689

o-Chloranil reacts with (diphenylacetylene)bis(triphenylphosphine)platinum(0) (**690**, L = PhC≡CPh) in benzene at room temperature to give diphenylacetylene complex **691**, which reacts with triphenylphosphine to yield **692**. By the same manner, it reacts with **690** (L = $HOCH_2C{\equiv}CCH_2OH$, (Et)(Me)(HO)CC≡C(OH)(Me)(Et), $CF_2{=}CH_2$, PhC≡CH) to afford the complex **692**.[440,441]

Pt(L)(PPh$_3$)$_2$

690



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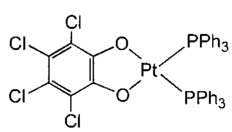
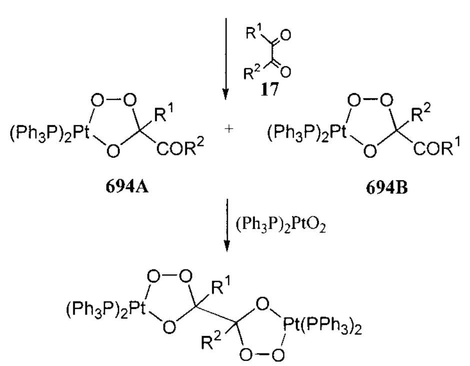


692

The reaction of unsymmetrical α-diketones **17** (R^1 = Et, R^2 = Me; R^1 = Ph, R^2 = Me; R^1 = *p*-$MeOC_6H_4$, R^2 = Me) with peroxobis(triphenylphosphine)platinum (**693**) in dichloromethane under nitrogen atmosphere furnishes the cyclic species as two isomers, **694A** and **694B**, in which just one of the carbonyl groups is incorporated into the cyclic part and the other remaining free, while in the case of symmetrical α-diketones **17** ($R^1 = R^2$ = Me, Ph) only one product, **694** ($R^1 = R^2$), is given.[442] Further addition of **693** to **694** produces the dinuclear species **695**, in which both carbonyl groups are coordinated.[442]

(Ph$_3$P)$_2$PtO$_2$

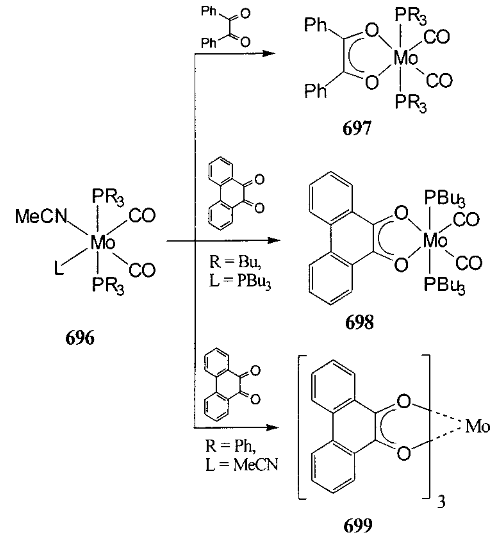
693



694A 694B

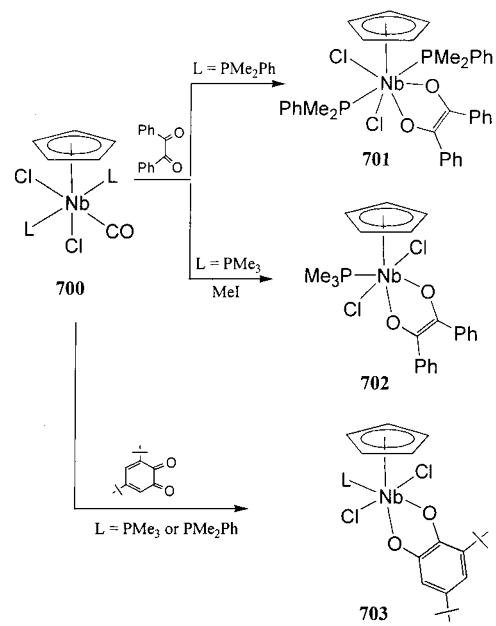
695

The phosphine molybdenum dicarbonyls **696** (R = Bu, Ph; L = MeCN) react with benzil in methanol to produce the complex **697**. Also, tributylphosphine complex **696** (R = Bu, L = PBu_3) reacts with phenanthrenequinone to give the *o*-quinone complex **698** still containing carbonyl ligands, whereas the triphenylphosphine complex **696** (R = Ph, L = MeCN) immediately reacts with phenanthrenequinone with loss of PPh_3 and CO to form the tris(phenanthrenequinone) complex **699** in quantitative yield.[443]



697 698 696 699

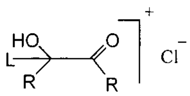
The reactions of monocyclopentadienylniobium(III) complexes **700** (L = PMe_2Ph, PMe_3) with 1 equiv of α-diketones and *o*-quinones led to different results, depending on L and the type of α-dicarbonyl compounds. When **700** (L = PMe_2Ph) reacts with benzil in toluene at room temperature for 20 h, the metalladienolate complex **701** is formed, whereas the same reaction of **700** (L = PMe_3) in the presence of methyl iodide gives the complex **702**.[444] By the same manner, 3,5-di-*tert*-butyl-*o*-benzoquinone with **700** (L = PMe_2Ph, PMe_3) furnishes the adduct **703**.[444]



701 700 702 703

On the other hand, biacetyl complexes formed from the reaction of biacetyl with **700** (L = PMe_3, PMe_2-

Ph) are unstable as in the benzil complex in the presence of L = PMe_3. In these cases, the free ligands attack the metalladienolate ring to give the corresponding phosphonium salts **704** (R = Me, L = PMe_3,

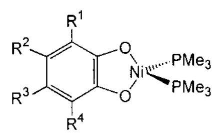


704

PMe_2Ph; R = Ph, L = PMe_3) and the unidentified products. All these compounds have been characterized by IR and ^1H, ^{13}C, and ^{31}P NMR spectroscopy. Moreover, the crystal structure of **704** (R = Me, L = PMe_2Ph), which was detected by X-ray diffraction, has the tetrahedral geometry around the phosphorus atom.[444]

The *o*-quinones 9,10-phenanthrenequinone, 1,2-naphthoquinone, and 3,5-di-*tert*-butyl-*o*-benzoquinone oxidatively substitute trimethylphosphine into nickel complex **705**,[445] affording the corresponding molecular compounds **706** [$R^1R^2 = R^3R^4 = (CH)_4$; $R^1R^2 = (CH)_4$, $R^3 = R^4$ = H; $R^1 = R^3$ = *t*-Bu, $R^2 = R^4$ = H] containing chelating dioxo ligands of the catecholate type.[446]

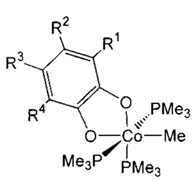
$Ni(PMe_3)_4$

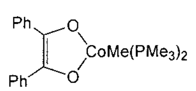


705 706

When the cobalt complex **707**[447] is used as the substrate to react with tetrachloro-*o*-benzoquinone, 3,5-di-*tert*-butyl-*o*-benzoquinone, and 9,10-phenanthrenequinone, the corresponding complex compounds **708** [$R^1 = R^2 = R^3 = R^4$ = H; $R^1 = R^3$ = *t*-Bu, $R^2 = R^4$ = H; $R^1R^2 = R^3R^4 = (CH)_4$] are formed, whereas with benzil gives the product **709**.[446]

$CoMe(PMe_3)_4$

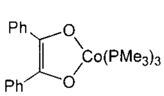


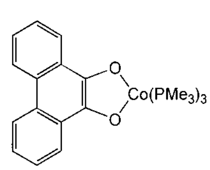


707 708 709

On the other hand, (ethene)tris(trimethylphosphine)-cobalt(0) **710**[448] reacts with benzil and 9,10-phenanthrenequinone to yield the paramagnetic catecholatocobalt(II) compounds **711** and **712**, respectively.[446]

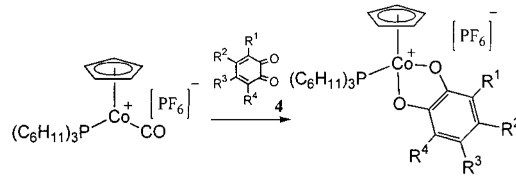
$Co(C_2H_4)(PMe_3)_3$





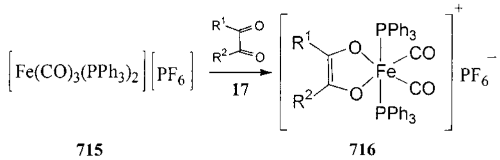
710 711 712

The addition of *o*-quinones **4** [$R^1 = R^2 = R^3 = R^4$ = Cl; $R^1R^2 = R^3R^4 = (CH)_4$; $R^1R^2 = (CH)_4$, $R^3 = R^4$ = H] to organotransition metal complex **713** in dichloromethane solution leads to the formation of paramagnetic quinone derivatives **714**. The ESR spectra of **714** suggest the unpaired electron to be localized mainly on the quinone ligand.[449]



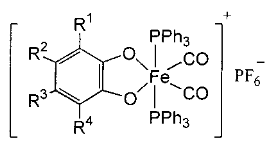
713 714

The iron complex **715**[450] reacts with α-diketones **17** ($R^1 = R^2$ = Me, Ph, 2-furyl) in dichloromethane or toluene at room temperature to yield the paramagnetic complexes **716**.[451]



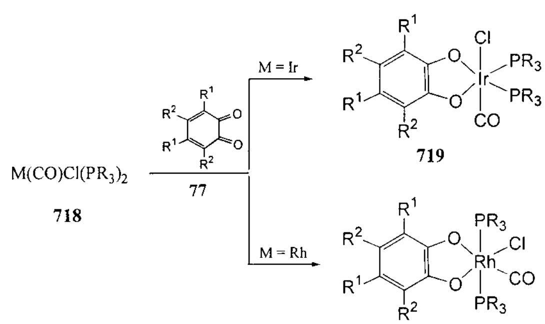
715 716

By the same manner, *o*-quinones **4** [$R^1 = R^2 = R^3 = R^4$ = Cl; $R^1R^2 = R^3R^4 = (CH)_4$; $R^1R^2 = (CH)_4$, $R^3 = R^4$ = H] react with iron complex **715** in dichloromethane to afford the complex **717**.[451]



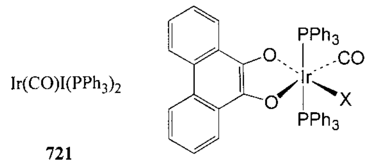
717

Tetrahalo-*o*-benzoquinones **77** ($R^1 = R^2$ = Cl, Br) react with iridium complexes **718** (M = Ir; PR_3 = PPh_3, PPh_2Me) in dichloromethane solution at 25 °C to yield the corresponding hexacoordinate complexes **719**, whereas the rhodium complexes **718** (M = Rh; PR_3 = PPh_3, PPh_2Me), with substituted *o*-quinones **77** ($R^1 = R^2$ = Cl; R^1 = *t*-Bu, R^2 = H), afford the isomers **720**. The stereochemistry of the addition products **719** and **720** has been determined through the examination of their ^1H NMR and far-infrared spectra.[432,452,453]



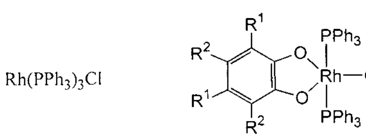
Under the mild conditions utilized for the addition of halogenated *o*-quinones to iridium complex **718** (M = Ir, PR_3 = PPh_3), the weaker oxidents 1,2-naphthoquinone, 9,10-phenanthrenequinone, acenaphthenequinone, and benzil do not appear to form adducts, although the thermal addition of 9,10-phenanthrenequinone and 1,2-naphthoquinone to this substrate has been reported to occur in refluxing benzene or by photoactivation.[431]

The iodo-substituted complex **721**, which is known to be more susceptible to oxidative addition than its chloro-substituted analogue, reacts readily at 25 °C with phenanthrenequinone to form the complex **722** (X = I).[431]



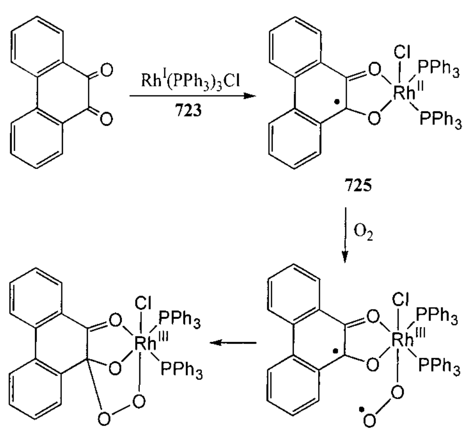
721 **722**

The addition of substituted *o*-quinones **77** ($R^1 = R^2$ = Cl; R^1 = *t*-Bu, R^2 = H) to tris(triphenylphosphine)-chlororhodium(I) (**723**) in dichloromethane solution produces the crystalline adduct of the corresponding biphosphine complex **724**, which in solution behaves as a monomeric nonelectrolyte and consequently has pentacoordinate structure, as confirmed by X-ray analysis.[431,453,454] Oxidative additions to rhodium complex **723** generally produce biphosphine complexes, because of the steric difficulties that would accompany the presence of a third phosphine ligand,[455−459] and a number of these biphosphine complexes are pentacoordinate.



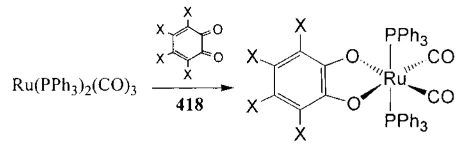
723 **724**

On the other hand, 9,10-phenanthrenequinone oxidized rhodium(I) complex **723** to unstable pentacoordinate rhodium(II) complex **725** in the semiquinone form, which undergoes further oxidation by aerial oxygen to generate the superoxo complex **726**, followed by obvious C−O bond formation between two close radical centers to afford the rhodium(III) complex **727**.[454] Its molecular structure has been determined by X-ray crystallography.



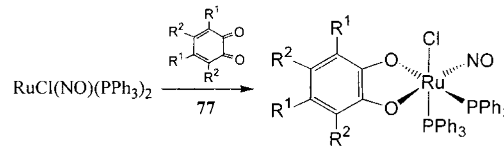
725 **726** **727**

The reaction of *trans*-ruthenium complex **728** with tetrahalo-*o*-benzoquinones (**418**, X = Cl, Br) has been shown to involve the loss of one carbonyl ligand, and the resulting products **729** contain a catecholate ligand bonded directly to ruthenium.[434,460] A similar product has been observed when the radical cation, $Ru(PPh_3)_2(CO)_3^+$ is reacted with *o*-chloranil.[461]



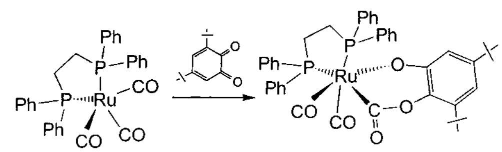
728 **729**

The ruthenium nitrosyl complex **730** is more reactive toward *o*-quinones **77** [$R^1 = R^2$ = Cl, Br; $R^1R^2 = (CH)_4$] than the carbonyl complexes of ruthenium and iridium, which gives the hexacoordinate complex **731**.[462]



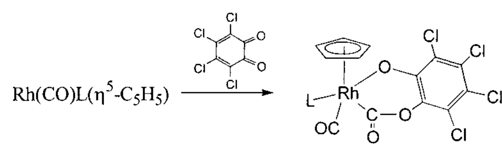
730 **731**

The oxidation of ruthenium complex **732** with 3,5-di-*tert*-butyl-*o*-benzoquinone in tetrahydrofuran affords the ruthenium−quinone adduct **733**, in which the quinone has formally added across the ruthenium−carbon bond of a metal carbonyl, resulting in a metallacyclic species with a carbonyl contained within the ring.[463]



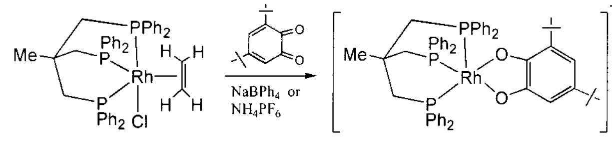
732 **733**

Another example of a similar reaction has been noted in which *o*-chloranil adds to the rhodium complexes **734** (L = CO, PPh_3) to form the products **735**.[464]



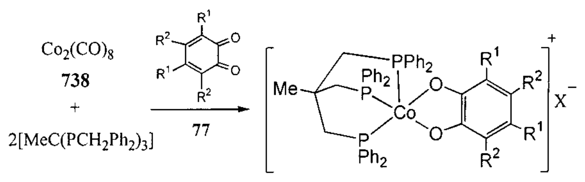
734 **735**

The coordinatively unsaturated Rh(III) catecholate complexes **737** (X = BPh_4, PF_6) have been synthesized by oxidative addition of 3,5-di-*tert*-butyl-*o*-benzoquinone to rhodium complex **736** in dichloromethane, followed by addition of either $NaBPh_4$ or NH_4PF_6 in ethanol.[465] Also, the monocationic cobalt(III) catecholate derivatives **740** [$R^1 = R^2$ = Cl; R^1R^2



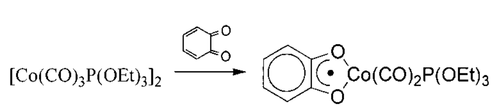
736 **737**

= $(CH)_4$; R^1 = *t*-Bu, R^2 = H] can be isolated as ClO_4^- or BPh_4^- salts from the reaction of the corresponding *o*-quinones **77** with a mixture of **738** and **739** in tetrahydrofuran, followed by addition of $(NBu_4)ClO_4$ or $NaBPh_4$.[466] The structure of **740** (R^1 = *t*-Bu, R^2 = H, X = BPh_4) was identified by X-ray analysis.[466]



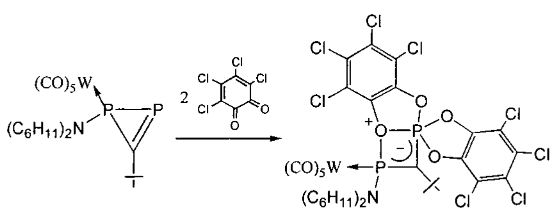
739 740

The irradiation of hexacarbonylbis(triethyl phosphite)dicobalt **741** with *o*-benzoquinone in toluene leads to the formation of a pentacoordinate complex **742**. A possible structure for **742** is one based on square pyramidal geometry about the cobalt atom, with the quinone molecule occupying two of the coordination sites at the pyramid base.[467] This would result in two possible isomers, one with the phosphite ligand in one of the two remaining basal positions, and one with the phosphite in the axial position. The observation of only one ^{31}P coupling constant indicates that only one of these isomers is formed under the experimental conditions involved, or that the radical is stereochemically nonrigid.[467]



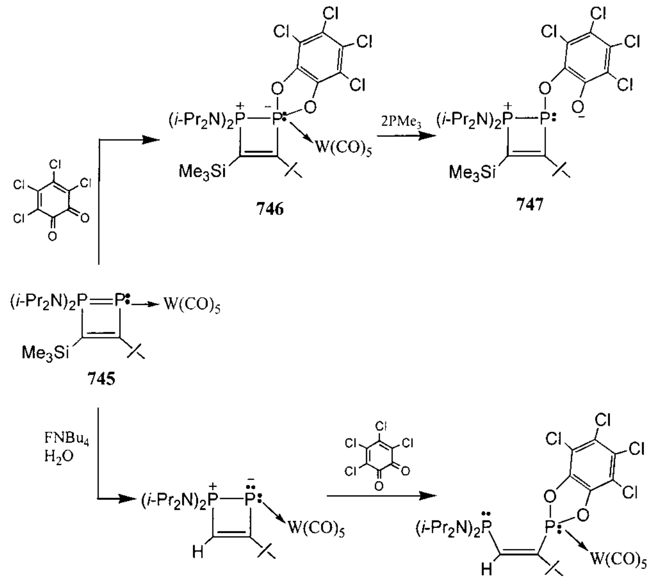
741 742

The subsequent addition of *o*-chloranil to 1*H*-diphosphirene complex **743** in dichloromethane at −40 °C, followed by warming to room temperature, gives rise to the 1:2 adduct **744**, in which the P−P bond has been cleaved. The molecular structure of bis-adduct **744** is detected by X-ray analysis.[468]



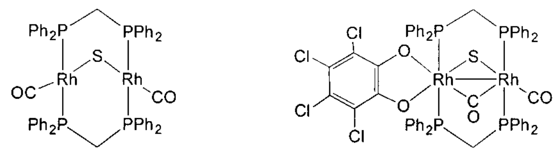
743 744

Addition of *o*-chloranil to the η^1-($1\sigma^4$,$2\sigma^2$-diphosphete)tungsten complex **745** in tetrahydrofuran at room temperature affords the η^1-($1\sigma^4$,$2\sigma^4$-diphosphete)-complex **746**, which reacts with 2 equiv of trimethylphosphine, leading to the zwitterionic $1\sigma^4$, $2\sigma^3$-diphosphete **747**. Cleavage of the Si−C bond of complex **745** with 1 equiv of tetrabutylammonium fluoride hydrate furnishes η^1-($1\sigma^4$,$2\sigma^2$-diphosphete)-complex **748**, which reacts with *o*-chloranil in pentane solution at −78 °C to room temperature to give the *cis*-1,2-diphosphinoalkene complex **749**. Single-crystal X-ray studies of derivatives **746**−**749** have been carried out.[394]



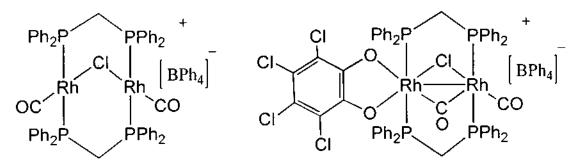
748 749

o-Chloranil is added to the binuclear rhodium complex **750** in dichloromethane to yield the product **751** with formation of a new Rh−Rh bond and conversion of a terminal carbon monoxide ligand to a bridging one.[469] The structure of **751** was elucidated by X-ray crystallography.[469]

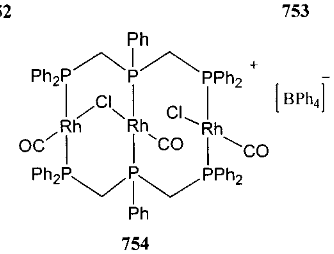


750 751

By the same manner, bi- and trinuclear rhodium complexes **752** and **754** react with *o*-chloranil to produce the adducts **753** and **755**, respectively.[469]



752 753



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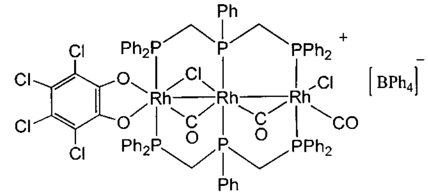

755

XV. Conclusion

This review has attempted to summarize the reactions of α-diketones and *o*-quinones with all phosphorus reagents. These reactions greatly extended synthetic possibilities in organic chemistry, led to the discovery of a number of extremely interesting types of reactions of organophosphorus compounds, and resulted in the introduction of many new features in the investigation of their mechanisms.

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