HETEROCYCLES BY CYCLOADDITION. XII.[1] CYCLOADDITION—EXTRUSION OF A MESOIONIC 1,3-DITHIOLIUM-4-OLATE AND A MESOIONIC OXAZOLIUM-5-OLATE WITH A PHOSPHIRENE. FORMATION OF SIX- AND FIVE-MEMBERED HETEROCYCLES¶

Tomoshige Kobayashi, Hidefumi Minemura, and Hiroshi Kato*

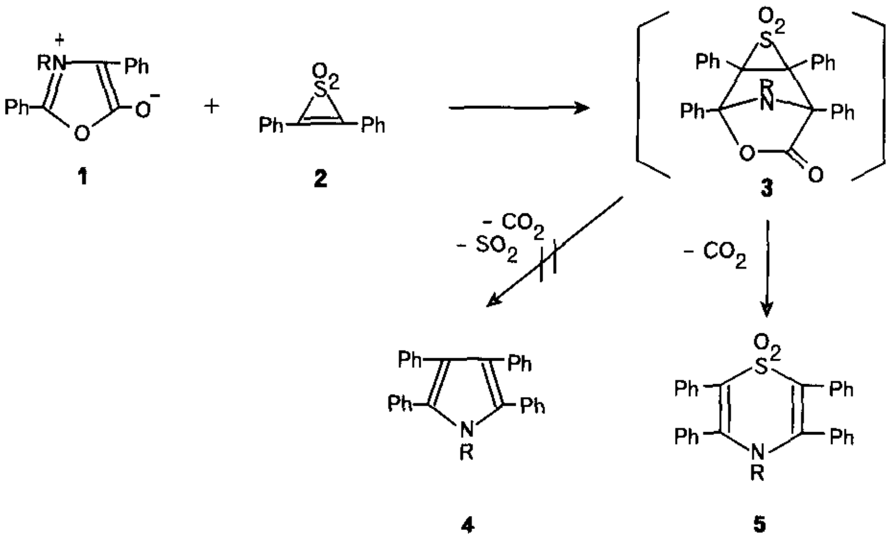
Department of Chemistry, Faculty of Science, Shinshu University,
Asahi, Matsumoto 390, Japan

Abstract — The reaction of a mesoionic dithioliumolate (**6**) with triphenylphosphirene (**7**) gave a cycloadduct (**8**). Pyrolysis of the cycloadduct (**8**) gave a 1,4-thiaphosphinine (**11**) and a thiophene (**9**). Acid treatment or photolysis of the cycloadduct (**8**) gave the thiophene (**9**) exclusively. The reaction of a mesoionic oxazolium-5-olate (**12**) and the phosphirene (**7**) gave a pyrrole (**15**) as the only isolable product.

Thanks largely to extensive works by Huisgen and his coworkers, 1,3-dipolar cycloaddition is now widely regarded as an important synthetic route to various heterocyclic systems.[2-6] During early stages of his series of studies on dipolar cycloadditions, it was pointed out that mesoionic compounds serve as excellent building blocks for construction of many heterocycles.[3-6] Through a series of investigations on cycloaddition reactions of mesoionic compounds,[7] we have shown that the reactions of this type can be useful for the preparation of not only five-membered aromatic heterocycles but also six-,[8,9] seven-,[10] eight-,[10] nine-,[11] and ten-membered[11] fully conjugated heterocycles.

We have found that the cycloaddition—extrusion reactions of mesoionic oxazolium-5-olates (**1**) with a thiirene dioxide (**2**) give 1,4-thiazine dioxides (**5**) by selective extrusion of carbon dioxide accompanied by cleavage of the three-membered ring.[9] There was no indication of the formation of pyrroles (**4**), which may have been formed by concomitant extrusion of both carbon dioxide and sulfur dioxide from the intermediate (**3**). We report here the cycloadditions of mesoionic compounds with 1,2,3-triphenyl-1*H*-phosphirene[12] (**7**).

¶ *Dedicated to Professor Huisgen on the occasion of his 75th birthday.*

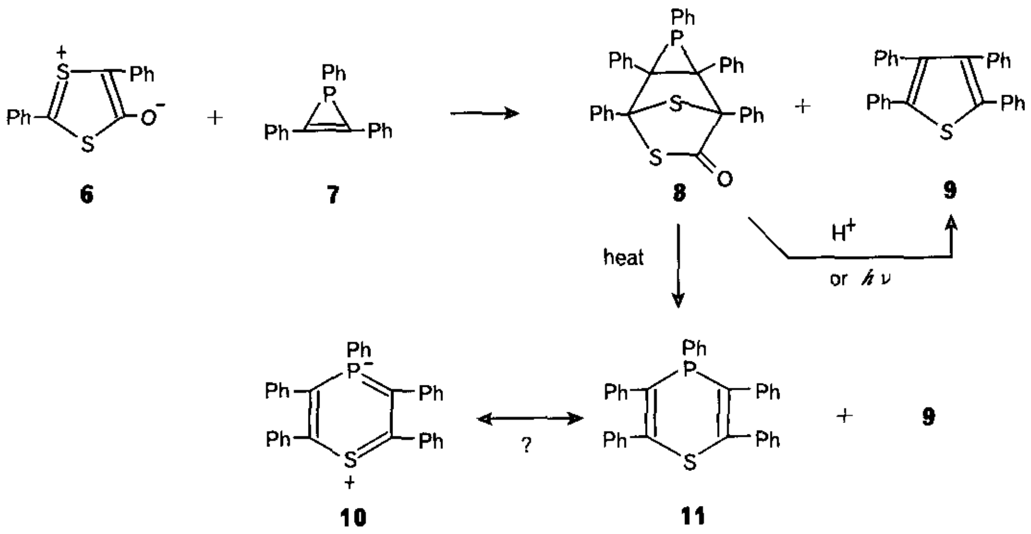


If these reactions proceed analogously, they should give fully unsaturated six-membered heterocycles with a phosphorus atom Such heterocyclic systems have been relatively little studied

RESULTS AND DISCUSSION

The reaction of the mesoionic 2,5-diphenyl-1,3-dithiolium-4-olate[13] (**6**) with 1,2,3-triphenyl-1*H*-phosphirene (**7**) at room temperature gave a cycloadduct, 1,2,3,4,5-pentaphenyl-3-phospha-7,8-dithiatricyclo[3.2 1.$0^{2,4}$]-octan-6-one (**8**), in 77% yield along with a small amount (4%) of tetraphenylthiophene (**9**). The yield of the cycloadduct (**8**) decreased to 20% when the reaction was performed at 40—50 °C. The structure of the cycloadduct (**8**) was supported by a ^{13}C-nmr signal at δ 200.6 and an infrared absorption at 1700 cm^{-1}, assignable to a strained thiol lactone,[11] and also by four sp^3-carbon nmr signals, which are split into doublets by the phosphorus atom. The ^{31}P-nmr of the cycloadduct (**8**) shows a peak at -255 ppm (from external H_3PO_4), and this value agrees with the expectation that the phosphorus atom will be shielded because it is part of a three-membered ring.[14] The cycloadduct (**8**) was isolated as a single stereoisomer although its stereochemistry could not be elucidated. The thiophene (**9**) was identified by comparison with an authentic specimen which was prepared by pyrolysis of tetraphenyl-1,4-dithiine.[15]

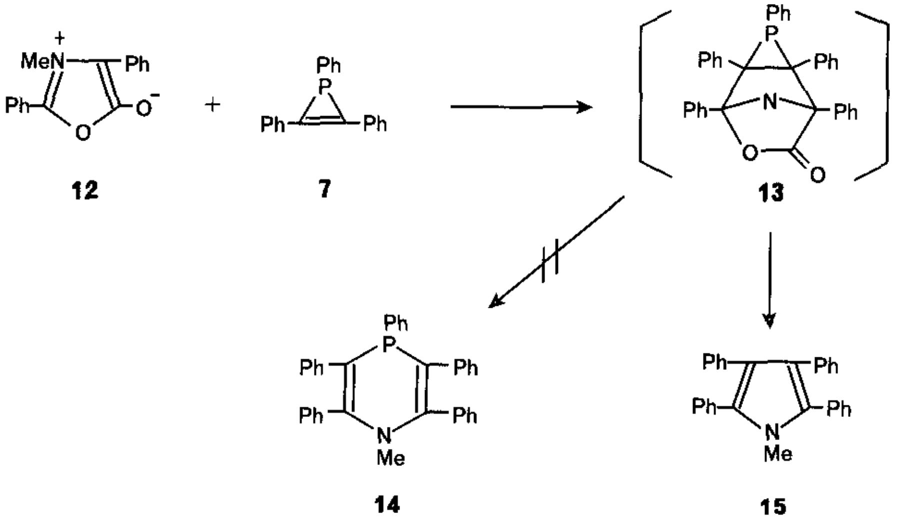
When the cycloadduct (**8**) was heated in xylene under reflux, the thiophene (**9**) (45%) and 2,3,4,5,6-pentaphenyl-4*H*-1,4-thiaphosphinine (**11**) (25%) were formed Hitherto, 4*H*-thiaphosphinines have been prepared in modest to fair yields by addition of phenylphosphine to di-1-alkynyl sulfides.[16] The ^{13}C-nmr spectrum of the thiaphosphinine (**11**) shows that the molecule has a plane of symmetry and that all the carbon atoms in the molecule are sp^2-hybridized. The mass spectrum of the thiaphosphinine (**11**) shows the molecular ion peak (base peak) and two prominent fragment peaks corresponding to ions formed by extrusion



of S and PhP respectively from the molecular ion. It is noteworthy that the ^{31}P-nmr signal of the thiaphosphinine (**11**) appears at -275 ppm (from H_3PO_4). The ^{31}P-nmr chemical shift values of 1,4-dihydro-1,4-diphosphinines[17] and 5,10-dihydrophenophosphazines[18] are within the ranges of -16 ~ -44 and -6 ~ -60 ppm respectively. This significant upfield shift of the ^{31}P-nmr of the thiaphosphinine (**11**) would suggest a strong shielding of the phosphorus nucleus probably due to a large contribution from the resonance structure (**10**). Calculations on 1,4-dithiines have suggested a varying degree of contribution from similar dipolar resonance structures.[19] However, PM3-MNDO calculation[20] on unsubstituted 4*H*-1,4-thiaphosphinine eliminated the possibility of a participation of the 3*d*-orbital of the phosphorus atom or a zwitterionic resonance structure. This calculation showed that the molecule adopts a flattened boat form as the most stable conformation: the dihedral angles of the C-S-C and C-P-C bonds deviate 2° and 8° respectively from the plane defined by the four ring-carbon atoms.

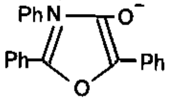
Irradiation of the cycloadduct (**8**) in benzene through a Pyrex filter afforded the thiophene (**9**) exclusively (81% yield). Although the thiaphosphinine ring system should be formally regarded as a (nonplanar) 8π-electron system, the thiaphosphinine (**11**) is a stable compound, and it was recovered unchanged after irradiation or being boiled in xylene. Therefore, the thiaphosphinine (**11**) is not the precursor of the thiophene (**9**) formed by photolysis or thermolysis, but the two products (**9**) and (**11**) are formed by independent competitive fragmentations of the cycloadduct (**8**). Treatment of the cycloadduct (**8**) with trifluoroacetic acid at room temperature also gave the thiophene (**9**) exclusively.

When a solution of the mesoionic 3-methyl-2,4-diphenyloxazolium-5-olate[21] (**12**) and the phosphirene (**7**) in acetonitrile was heated under reflux, 1-methyl-2,3,4,5-tetraphenylpyrrole (**15**) was isolated as the sole product (45% yield). The yield of the pyrrole (**15**) decreased to 15% when the oxazoliumolate (**12**) was formed *in situ*



in the reaction medium. The pyrrole is expected to be formed from the unisolable cycloadduct (**13**) by extrusion of CO$_2$ and PhP either in a concerted fashion or stepwise *via* the 1,4-phosphazine intermediate (**14**). There is another possible path to the formation of the thiophene (**9**) and the pyrrole (**15**): the phosphirene (**7**) may decompose under the reaction conditions to diphenylacetylene, and cycloaddition—extrusion reaction of the latter with the mesoionic compounds would give the five-membered heterocycles. This possibility can be excluded because it was found that the phosphirene (**7**) decomposed to diphenylacetylene only to an extent of 2% after being heated under reflux for 10 h in acetonitrile. Moreover, it has been reported that the dithiolium-olate (**6**) did not react with diphenylacetylene.[13] We have confirmed that the reactions of diphenylacetylene with the mesoionic compounds (**6**) and (**12**) proceeded sluggishly, and gave only poor yields of the thiophene (**9**) (13 %; boiling in xylene; 58 h) and the pyrrole (**15**) (21%; boiling in acetonitrile; 10 h).

We have also studied the reactions of the phosphirene (**7**) with the mesoionic 2,3,5-triphenyloxazolium-4-olate[22] (**16**) and 4-phenyl-1,3,2-oxathiazolium-5-olate[23] (**17**) The reaction with the oxazolium-4-olate (**16**) gave *O*-benzoylmandelanilide (**18**) (75% yield) as the only isolable product, which was probably formed by hydrolysis of the oxazolium-4-olate (**16**) during work-up.[22] The reaction with the oxathiazoliumolate (**17**) resulted in an intractable complex mixture.



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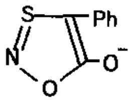

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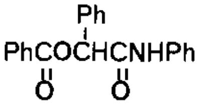

$\mathrm{Ph\underset{\underset{O}{\|}}{C}O\overset{\overset{Ph}{|}}{C}H\underset{\underset{O}{\|}}{C}NHPh}$

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EXPERIMENTAL

Melting points were determined on a Yanagimoto hot-stage and are not corrected Infrared (KBr disk) and ultraviolet spectra were measured on a Hitachi 345 and a Shimadzu UV-260 spectrophotometer respectively. ^{1}H (90 MHz) and ^{13}C (22.5 MHz) nmr (CDCl$_3$ solution) spectra were recorded with a JEOL JNM-FX-90Q spectrometer with tetramethylsilane as an internal standard, and ^{31}P-nmr (36.2 MHz) spectra were measured with the same spectrometer by the use of 85% H$_3$PO$_4$ as an external standard. Mass spectra were measured with a Shimadzu GCMS-QP1000EX spectrometer at an ionization potential of 70 eV. Elementary analyses were performed with a Perkin-Elmer Model 240 apparatus. All yields are based on isolated products with sufficient purity

Cycloaddition of the Dithioliumolate (6) with the Phosphirene (7). A solution of the dithioliumolate (**6**)[13] (1.13 g, 4.2 mmol) and the phosphirene (**7**)[12] (1.86 g, 6.5 mmol) in benzene (50 ml) was allowed to stand in the dark at room temperature for 46 days under nitrogen. The solution was concentrated and acetone was added The crystals which separated out were collected and washed with acetone to give the cycloadduct (**8**) (1.80 g, 77%). Colorless needles (from acetonitrile), mp 206—207 °C (decomp.); uv$_{max}$ (EtOH) (log ε) 276 (3.71), 284 (3.63), and 323 nm (2.68); ir 1700 cm^{-1} (C=O); ^{1}H-nmr δ 6.23—7.21 (m), ^{13}C-nmr δ 59.6 (d, $^{1}J_{\text{C-P}}$ 31 Hz), 68.3 (d, $^{1}J_{\text{C-P}}$ 31 Hz), 79.2 (d, $^{2}J_{\text{C-P}}$ 13 Hz), 82.4 (d, $^{2}J_{\text{C-P}}$ 15 Hz), 126.1—137.6, and 200.6 (d, $^{3}J_{\text{C-P}}$ 4 Hz); ^{31}P-nmr δ -255; ms *m/z* (rel. intensity) 496 (M^{+} - SCO, 33) and 388 (M^{+} - SCO - PhP, 100). Anal. Calcd for C$_{35}$H$_{25}$OPS$_2$: C, 75.42; H, 4.28. Found: C, 75.52; H, 4.53 Separation of the filtrate on silica gel (hexane—dichloromethane, 1 : 3) gave the thiophene (**9**) (70 mg, 4%), mp and mixed[15] mp 183—185 °C (lit.,[24] mp 184 °C).

Acid Treatment of the Cycloadduct (8). A solution of the cycloadduct (**8**) (278 mg, 0.5 mmol) and trifluoroacetic acid (0.6 ml, 0.8 mmol) in dichloromethane (3 ml) was stirred at room temperature for 5 days. The mixture was washed with aq. 3% sodium bicarbonate, dried (Na$_2$SO$_4$), and concentrated. The residue was washed with acetonitrile to give the thiophene (**9**) (180 mg, 93%) identical with an authentic specimen.[15]

Pyrolysis of the Cycloadduct (8). A solution of the cycloadduct (**8**) (2.12 g, 3.8 mmol) in xylene (30 ml) was refluxed for 68 h under nitrogen. The solution was concentrated and the residue was separated on column chromatography (silica gel, benzene) to give the thiophene (**9**) (665 mg, 45%), identical with an authentic specimen,[15] and the thiaphosphinine (**11**) (470 mg, 25%). Yellow needles (from acetonitrile), mp 196—198 °C; uv$_{max}$ (EtOH) (log ε) 243 (4.43) and 316 nm (3.85); ir 3070, 1475, 1430, 1090, and 1025 cm^{-1}; ^{1}H-nmr δ 6.86—7.14 (20H, m), 7.24—7.49 (3H, m), and 7.88—8.14 (2H, m); ^{13}C-nmr δ 126.7—

150.8, ^{31}P-nmr δ -275; ms *m/z* (rel. intensity) 496 (M^+, 100), 464 (M^+ - S, 23), and 388 (M^+ - PhP, 81). Anal. Calcd for $C_{34}H_{25}PS$: C, 82.23; H, 5.07. Found· C, 82.28; H, 4 89.

Irradiation of the Cycloadduct (8). A deaerated solution of the cycloadduct (**8**) (278 mg, 0.5 mmol) in anhydrous benzene (150 ml) was irradiated internally for 4 h with a 100-W high-pressure mercury lamp through a Pyrex filter under 20 °C and under an atmosphere of argon. The solution was concentrated and the crystals which separated out on addition of acetonitrile were collected to give the thiophene (**9**) (158 mg, 81%), identical with an authentic specimen.[15]

Reaction of the Mesoionic Oxazolium-5-olate (12) with the Phosphirene (7). A solution of the oxazoliumolate (**12**)[21] (160 mg, 0.6 mmol) and the phosphirene (7) (180 mg, 0 6 mmol) in anhydrous acetonitrile (5 ml; 0.2 ml of acetic anhydride had been added previously) was refluxed for 10 h under an atmosphere of nitrogen The crystals which separated out on cooling were collected and washed with acetonitrile to give 1-methyl-2,3,4,5-tetraphenylpyrrole (**15**) (104 mg, 45%), mp and mixed mp 210—212 °C (lit.,[4] 210—211 °C).

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