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1, 3, 4-옥사티아졸-2-온과 1, 2, 4-디티아졸-3-온의 3가인 화합물과의 탈황반응에 관한 연구

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Studies on the Desulfurization of 1, 3, 4-Oxathiazol-2-one and 1, 2, 4-Dithiazol-3-one with Trivalent Phosphorus Compounds

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요 약. 5-아릴-1, 3, 4-옥사티아졸-2-온을 트리에틸포스파이트와 반응시키면 탈황반응에 의해 벤조니트릴과 에틸포스포로티오에이트가 66~94 % 수득율로 얻어졌다. 다른 3가의 인화합물 즉, 트리메틸포스파이트, 트리에틸포스핀, 그리고 트리페닐포스핀들과도 같은 탈황반응이 관찰되었다. 그러나 트리페닐포스파이트와는 전혀 반응하지 않았다. 5-아릴-1, 3, 4-디티아졸-2-온을 트리페닐포스핀과 반응시키면 티오아실 이소시아네이트가 얻어졌다. 이것은 에테르에서 자체적으로 분해되어 벤조니트릴로 변하게 되나 클로로포름에서는 안정하다. 이 두 반응에서 관찰되는 탈황반응은 인이 고리속으로 들어가 고리를 늘인후 분자내에서의 자리옮김 반응에 의해 일어나는 것이라 생각된다. 클로로포름에서 안정한 티오아실 이소시아네이트는 이민과 1, 4-고리화 첨가반응을 일으켜 티아다이아지논을 생성하였다.

ABSTRACT. The reactions of various 5-aryl-1, 3, 4-oxathiazol-2-ones with triethylphosphite resulted in the formation of the corresponding benzonitriles and ethylphosphorothioate by desulfurization reaction in 66~94 % yields. 5-(4-Nitrophenyl)-1, 3, 4-oxathiazol-2-one was also reacted with trimethylphoshite, triethylphosphine, and triphenylphosphine to give 4-nitrobenzonitrile. But it did not react with triphenylphosphite. The reaction of 5-(4-bromophenyl)-1, 2, 4-dithiazol-3-one with triphenylphosphine resulted in the formation of 4-bromothiobenzoyl isocyanate and triphenylphoshine thioxde. The thioacyl isocyanate was fragmented into nitrile in ether but was stable in chloroform. This desulfurization reaction observed in each reaction may proceed by the intramolecular rearrangement after insertion of the phosphorus compound into the ring. The stable thioacyl isocyanate in chloroform reacted with imine to give 1, 3, 5-thiadiazin-4-one via 1, 4-cycloaddition reaction.

INTRODUCTION

The heterocyclic compound, 5-aryl-1, 3, 4-oxathiazol-2-one was introduced first by Senning in 1965[1]. It has been developed at an ever increasing pace[2] since then. Until recently,

considerable attention has been focused on the heterocyclic compounds such as 5-aryl-1, 3, 4-oxathiazol-2-one and 5-aryl-1, 2, 4-dithiazol-3-one because they are highly valuable intermediates for the synthesis of other heterocyclic compounds. Howe[3] reported the evidence for the production of nitrile sulfide as a reactive intermediate in the thermolysis of 1, 3, 4-oxathiazol-2-ones and reaction of nitrile sulfide with acetylenic esters to form isothiazole carboxylates in preparatively significant reactions. Dipolar cycloaddition of arenecarbonitrile sulfides to various olefins and benzonitriles were also decribed by Howe[4] *et als.* 1, 2, 4-Dithiazol-3-one is also the reactive intermediate for the synthesis of new classes of heterocyclic compound, 1, 3, 5, -thia-diazin-4-one[5].

In this work, the reaction of 5-aryl-1, 3, 4-oxathiazol-2-one with the reactive trivalent phosphorus compounds such as phosphites and phosphines was examined first because there has been no previous report on such reaction. And the reaction of 5-(4-bromophenyl)-1, 2, 4-dithiazol-3-one with triphenylphosphine was reinvesitigated to compare with the reaction of 5-aryl-1, 3, 4-oxathiazol-2-one with trivalent phosphorus compounds. From the new observations in such reactions its possible reaction mechanism is suggested and discussed.

EXPERIMENTAL

Materials

Pyridine and triethylamine (Wako) were refluxed with calcium oxide, distilled, and kept over sodium hydroxide. Trichloromethanesulfenyl chloride (Aldrich), triethylphine (Aldrich) in isopropanol (67% wt.), triphenylphosphine (Aldrich), triphenyl-phosphite (Aldrich), and all of the benzamide derivatives (Aldrich) were used without further purification. Triethylphosphite (Aldrich) and triethylphosphite (Aldrich) were purified by treatment with sodium metal followed by vacuum distillion. ^{1}H NMR spectra were recorded on a Varian T-60A spectrometer, using TMS as an internal standard. IR spectra were measured with Perkin-Elmer model 283B and 267 grating infrared spectrometers using NaCl or KBr pellet. Melting points were determined with a Fisher-Johns melting point apparatus and are uncorrected.

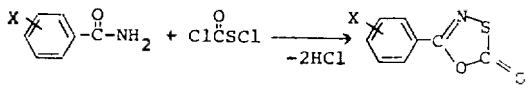
Preparation of 5-Aryl-1, 3, 4-oxathiazol-2-ones

Chlorocarbonylsulfenyl chloride was prepared according to the method introduced by Zumach and Kühle[6]. A mixture of 0.01 mole of benzamide and 0.03 mole of chlorocarbonylsulfenyl chloride in 50m*l* of toluene was placed in a 100m*l* round bottomed flask fitted with a reflux condenser. The slightly soluble amide in toluene was soluble at an increased temperature of 60 °C. But 2-nitrobenzamide was not soluble in toluene at about 100°C. This difficulty was eliminated by using more polar solvent such as 1, 4-dioxane. Then the solution was heated to reflux for about one day. IR was used to monitor the disappearance of the amide peak. The hydrogen chloride evolved during the reaction was trapped in about 20 % sodium hydroxide solution. When the reaction was completed, the reaction mixture was allowed to cool slowly. The crude white or light yellow solid was precipitated after 1~2 hours at 0°C, filtered, and then recrystallized from appropriate solvent (benzene, toluene, THF, methanol, and ethanol *etc.*). The results obtained are summerized in Table 1.

Reaction of 5-Aryl-1, 3, 4-oxathiazol-2-ones with Triethylphosphite

A mixture of 0.01 mole of oxathiazolone and 0.01 mole of the purified triethylphosphite in 50m*l* of the toluene was placed under nitrogen

Table 1. Preparation[a] of 5-aryl-1, 3, 4-oxathiazol-2-one from benzamide and chlorocarbonylsulfenyl chloride.

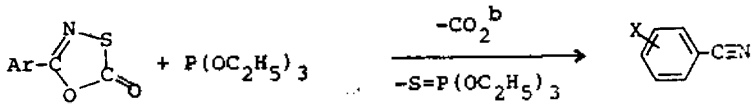


1a-h 2a-h

Aryl Group in 2	IR(cm^{-1}) C=O	C=N	Yield(%)[b]	mp (°C)	(*lit.*[7]) (°C)
2a, Phenyl (benzene)[c]	1745	1560	74	70-71	(68.5-70)
2b, 2-Nitrophenyl[d] (toluene)	1755	1570	71	111-112	(111-113)
2c, 3-Nitrophenyl (benzene)	1720	1585	79	95-97	(96.5-98)
2d, 4-Nitrophenyl (THF)	1750	1570	85	163-164	(163-164)
2e, 3-Methoxyphenyl (methanol)	1750	1565	67	93-94	(93-94)
2f, 4-Methoxyphenyl (methanol)	1750	1565	66	98-99	(99-101)
2g, 4-Bromophenyl (ethanol)	1730	1550	90	140-142	
2h, 4-Chlorophenyl (ethanol)	1630	1550	89	127-128	(127-130)

[a]Reaction conditions; 1/ClC(=O)SCl=1/3 mole ratio, 100-110°C, 24 hr in toluene; [b]Yields are for the recrystallization product based on the amount of benzamide; [c]In parenthesis are recrystallization solvents; [d]1, 4-Dioxane was used as a solvent.

Table 2. Reaction[a] of 5-aryl-1, 3, 4-oxathiazol-2-ones with triethylphosphite.



2b-d, f-g 3b-d, f-g

X in 3	IR(cm^{-1}), C≡N	Yield[c] (%)	mp (°C)	(*lit.*[8]) (°C)
3b, 2-Nitro (n-hexane)	2230	93	113-114	(114.8)
3c, 3-Nitro (ethyl ether)	2225	94	118	(117-118)
3d, 4-Nitro (ethyl ether)	2235	83	143-145	(147)
3f, 4-Methoxy (methanol)	2245	66	61-62	(59-61)
3g, 4-Bromo (pet. ether)	2220	92	114-114.5	(113)
3h, 4-Chloro (pet. ether)	2215	85	91-92	(91-92)

[a]Reaction conditions; 2/phosphite=1 mole ratio, 110°C, 24 hr in toluene under N_2; [b]The ethyl phosphorothioate and carbon dioxide were identified solution respectively; [c]Yields are for the recrystallization product; [d]In parenthesis are recrystallization solvents.

atmosphere in a 100m*l* 3-neck round bottomed flask fitted with reflux condenser which was connected into a saturated barium hydroxide solution. The mixture gave a homogeneous solution at about 50°C with moderate stirring. Then the solution was heated at about 110°C to reflux for about one day. When the reaction was completed, the solution was allowed to room temperature, and distilled under reduced pressure. The viscous residue probably due to the

undistilled solvent and/or ethyl phosphorothioate was concentrated by rotary evaporator. Recrystallization of the crude product from the appropriate solvent (*n*-hexane, ethyl ether, methanol, and pet. ether *etc.*) gave the corresponding benzonitrile. The results obtained are summerized in *Table* 2.

Reaction of 5-(4-Nitrophenyl)-1, 3, 4-oxathiazol-2-one with Trivalent Phosphorus Compounds

Reaction with Trimethylphosphite. 2.242g (0.01 mole) of 5-(4-nitrophenyl)-1, 3-4-oxathiazol-2-one was reacted with 1.24g (0.01 mole) of trimethylphosphite at 75~80°C for about 20 hours. The yield was 1.111g (75 %) by recrystallization from ethyl ether.

Reaction with Triphenylphosphite. 2.242g (0.01 mole) of 5-(4-nitrophenyl)-1, 3, 4-oxathiazol-2 one was reacted with 3.103g (0.01 mole) of triphenylphosphite at 110°C for 24 hours. But all of the starting material was recovered (99 %). Despite of the prolonged reaction time, no reaction was observed.

Reaction with Triethylphosphine. 2.242g (0.01 mole) of 5-(4-nitrophenyl)-1, 3-4-oxathiazol-2-one was reacted with 1.181g (0.01 mole) of triethylphosphine at 100~110°C for 24 hours. The yield was 1.387g (93%) by recrystallization from ethyl ether.

Reaction with Triphenylphosphine. 2.242g (0.01 mole) of 5-(4-nitrophenyl)-1, 3, 4-oxathiazol-2-one was reacted with 2.263g (0.01 mole) of triphenylphosphine at 100~110°C for 12 hours. After removal of toluene by rotary evaporator, recrystallization from ethyl alcohol gave a white needle like product which was identified as triphenylphosphine thioxide by its ^{1}H NMR and IR spectra. The filterate was concentrated again and recrystallized from ethyl ether to yield 1.452g (98 %) of 4-nitrobenzonitrile.

Preparation of 5-(4-Bromophenyl)-1, 2, 4-dithiazol-3-one from 4-Bromothiobenzamide

The direct displacement of oxygen by sulfur using phosphorus pentasulfide as the thiating agent was performed according to the method introduced by Klingsberg and Papa[9] using pyridine as a solvent. Thus using this method 4-bromethiobenzamide was obtained from 4-bromobenzamide in 88% yield. A 100m*l* round bottomed flask fitted with a calcium chloride guard tube and a dropping funnel was packed in a dry ice-acetonitrile bath (−40°C). The flask was charged with 1.312g (0.01 mole) of chlorocarbonyl-sulfenyl chloride in 15m*l* THF. To the solution was added the yellow solution of 2.161g (0.01 mole) of 4-bromothiobenzamide in 30m*l* THF slowly through the dropping funnel. At the moment of dropping, the solution turned red. When all the solution of thioamide had been added, the mixture was stirred for additional 30 minutes. Gradually colorless product was separated. Increasing the reaction temperature to −20°C (a carbone tetrachloride-dry ice bath) and then cooling again to −40°C, 0.02 mole of triethylamine in 10m*l* THF was introduced into the solution slowly. Strong exothermic reaction was observed. When the reaction was completed, the mixture was allowed to room temperature and the triethylamine-HCl salt was filtered and washed with THF. The combined filterate was concentrated by rotary evaporator, and recrystallized from *n*-hexane to yield 2.329g (85 %) of a yellow product. mp: 150~153°C, NMR($CDCl_3$): δ 7.6 (*d*, 2H, ArH, J=9Hz), 8.0(*d*, 2H, ArH, *J*= 9Hz), IR(KBr) : 3040(C-H), 1687(C=O), 1510(C=N) cm^{-1}.

Reaction of 5-(4-Bromophenyl)-1, 2, 4-dithiazol-3-one with Triphenylphosphine

A 100m*l* round bottomed flask, fitted with a dropping funnel was packed in an ice bath

(0°C) under nitrogen. The flask was charged with the solution of 1.0 mmole dithiazolone in 15m*l* chloroform. To the solution was added the solution of 1.0mmole triphenylphosphine in 15m*l* chloroform slowly through the dropping funnel with moderate stirring. When all of the phosphine had been added, the reaction mixture turned violet. After stirring the solution for 1 hour, the reaction mixture was allowed to −78°C(acetone-dry ice bath). The triphenylphosphine thioxide was separated and filtered immediately by suction apparatus, and washed with cold chloroform. The combined filterate was concentrated by rotary evaporator below 20°C. Nearly all of the triphenylphosphine thioxide was separated by doing this operations three times. The resultant concentrated filterate was run on IR spectrometer giving the absorption bands at 3080 (C-H) and 2230 (N=C=S)cm^{-1}. But in ethyl ether, the product according to the above procedure was 4-bromobenzonitrile(3g). And the other product, triphenylphosphine thioxide was characterized by its mp. and spectral data.

Reaction of 4-Bromothiobenzoyl Isocyanate with Benzalaniline

Benzalaniline was prepared from benzaldehyde and aniline by the usual method[10]. A 100m*l* round bottomed flask fitted with a dropping funnel was packed in water bath at room temperature. The flask was charged with the solution of 2.74g(0.01 mole) of 5-(4-bromophenyl)-1, 2, 4-dithiazol-3-one in 30m*l* CH_2Cl_2. To the solution was added the mixture of 2.620g (0.01 mole) of triphenylphosphine and 1.812g(0.01 mole) of benzalaniline in 30m*l* of CH_2Cl_2 slowly through the dropping funnel under nitrogen. An additional stirring for about 30 minutes was required. And then the mixture was concentated to 10m*l* by rotary evaporator below 20°C. The product was separated by preparative TLC (1mm×20cm, Wakogel GF_{254}) and extracted with methanol. The extract was fully concentrated by rotary evaporator, filtered, and washed well with chloroform. The crude product obtained by concentrating the filterate was recrystallized from n-hexane to yield 1.047 g(23 %) of a brown crystal. mp: 193∼195°C, NMR($CDCl_3$): δ 6.1(*s*, 1H, CH), 7.3(*m*, 8H, ArH), 7.5(m, 3H, ArH), 7.9(3H, ArH), IR (KBr): 3080(C-H), 1655(C=O), 1495(C=N) cm^{-1}.

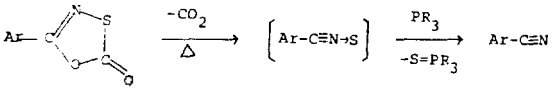
RESULTS AND DISCUSSION

The reaction of benzamide with the bifunctional chlorocarbonylsulfenyl chloride was monitored by the disappearance of amide peak(3200 ∼3500cm^{-1}) in IR spectrum. The synthesized 5-aryl-1, 3, 4-oxathiazol-2-one in 66-90 % yields have the characteristic absorption bands at 1550 ∼1585cm^{-1} (C=N) and 1720∼1755cm^{-1}(C=O).

The reaction of 5-aryl-1, 3, 4-oxathiazol-2-ones with triethylphosphite under nirogen at toluene reflux temperature for about one day resulted in the formation of the corresponding benzonitrile, ethyl phosphorothioate, and carbon dioxide. The ring substituted benzonitriles gave their characteristic absorption band in IR at 2215∼2245cm^{-1}(C≡N). The yields were 66∼94 %.

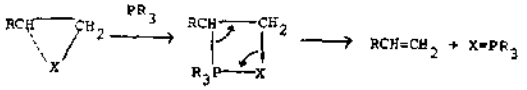
The desulfurization mechanism of this reaction can be considered in some ways. The desulfurization similiar with this reaction has already been studied. in the reaction of 1, 2-thionocarbonates with a phosphite ester, it was postulated by a concerted, cycloelimination mechanism for the product forming step. In case of 5-aryl-1, 3, 4-oxathiazol-2-one, the direct desulfurization by triethylphosphite is impossible. Considering the hypothetical isomerization of 1, 3, 4-oxathiazol-2-one into thionocarbonate and following desulfurization by trie-

thylphosphite can explain the observed reaction. But this hypothesis seems to be improbable because no coupling product was obtained. Moreover addition of benzaldehyde gave no inhibition effect[11] on nitrile formation. In the reaction of 5-aryl-1, 3, 4-oxathia-zol-2-one with nitrile, triple bond, and olefin in many significant reactions[12] via nitrile sulfide for 1, 3-cycloaddition, the reaction temperature was over 190°C. But even at room temperature for 24 hours benzonitrile was obtained in 24% yield in the reaction of 5-(4-nitrophenyl)-1, 3, 4-oxathiazol-2-one with triethylphosphite. So thermolysis to nitrile sulfide seems to be unrea-



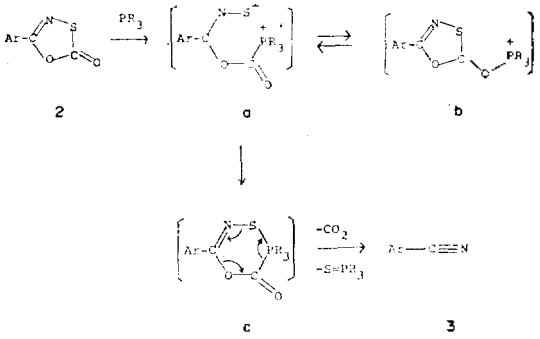
sonable mechanism at toluene reflux temperature even though trivalent phosphorus compound may enhance the next desulfurization step.

And the desulfurization of heterocyclic five-membered ring[13], epoxides[14], and sulfoxides[15] by trialkyl phosphite was examined already. The most favored reaction is the elimination of the oxygen or sulfur of the three membered ring and formation of the olefin.



(X=O, S)

The most plausible desulfurization mechanism in reaction of 1, 3, 4-oxathiazol-2-one with triethylphosphite is the intramolecular rearrangement after insertion of phosphorus componnd into the ring. Even thongh the nucleophilic attack takes place in C-atom of the carbonyl group, it (**b**) can be existed at equilibrium with (**a**) which is attacked directly in O-atom of the carbonyl group. After cyclization of (**a**), the intermediate (**c**) proceeds the concerted intramolecular rearrangement to form the benzonitrile, ethyl phosphorothioate, and carbon dioxide.



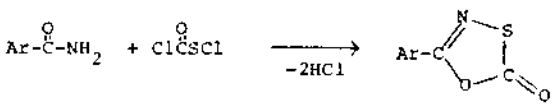
Reaction of 5-(4-nitrophenyl)-1, 3, 4-oxathiazol-2-one with trimethylphosphite at 75~80°C for 20 hours gave 4-nitrobenzonitrile in 75% yield. The methyl phosphorothioate was characterized by its ^{1}H NMR and IR spectra. The stretching absorption band of P=S in IR appeared at 810~830cm^{-1}(very strong and broad). Similar reaction with triphenylphosphite was not proceeded despite of prolonged reaction time (48 hours) probably due to the low nucleophilicity and steric hindrance of triphenylphosphite compared with other trivalent phosphorus compounds. Reaction with triethyl-and triphenylphosphine resulted also in the formation of 4-nitrobenzonitrile in good yields (93% and 98% respectively). These results are summerized in *Table* 3.

Different mode of cyclization pattern was observed in the reaction of benzamide and thiobenzamide with the bifunctional chlorocarbonylsulfenyl chloride. These differences in condensation could be deducted by the evidence that was based on the difference in IR spectra between **2** and **5**. The differences shown in *Table* 4 occur in the frequency shifts becasue of the unconjugation and conjugation between two double C=N and C=O absorption bands

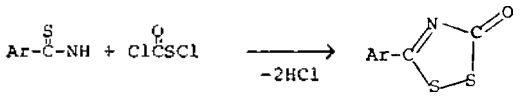
Table 3. Recation[a] of 5-(4-Nitrophenyl)-1, 3, 4-oxathiazol-2-one with some trivalent phosphorus compounds.

Trivalent Phosphorus Compound	Reaction Temp. (°C)	Reaction Time(hr.)	Yield (%)
$P(OC_2H_5)_3$	100	24	83
$P(OCH_3)_3$	75~80	20	75
$P(OC_6H_5)_3$	110	24~48	—
$P(C_2H_5)_3$	100~110	24	93
$P(C_5H_5)_3$	100~110	12	98

[a]Reaction products were 4-nitrobenzonitrile, $S=PR_3$, and CO_2.



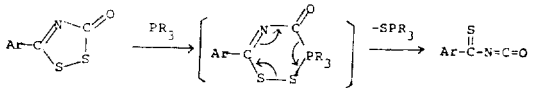
1 2



4 5

in 1, 3, 4-oxathiazol-2-one (**2**) and 1, 2, 4-dithiazol-3-one (**5**) respectively, and more significantly in the reversal of the relative intensities of the C=N and C=O absorption bands. These differences are summerized in *Table* 4.

The reaction of 5-(4-bromophenyl)-1, 2, 4-dithiazol-3-one with triphenylphosphine at 0°C in chloroform under nitrogen was performed to study the IR spectrum of the unstable thioacyl isocyanate which is an intermediate of the 1, 4-cycloaddition reaction with imine[5]. The desulfurization to yield thioacyl isocyanate(**6**) in



(Ar=4-BrPh) (R=Ph) 6

5

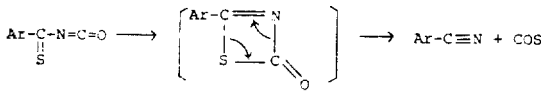
chloroform can also be explained by the

Table 4. Difference of frequency and absorption intensity in IR between 1, 3, 4-oxathiazol-2-one and 1, 2, 4-dithiazol-3-one (C=N and C=O absorption bands).

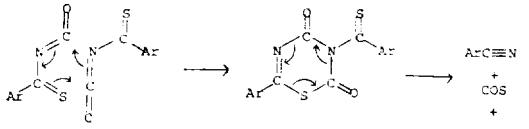
Compound	C=N(cm^{-1})	C=O(cm^{-1})
1, 3, 4-oxathiazol-2-one[a]	1550~1585 (*m* or *s*)[c]	1720~1755 (*s* or *vs*)
1, 2, 4-dithiazol-3-one[b]	1485~1520 (*s* or *vs*)	1655~1710 (*m* or *s*)

[a]The data from the synthesized 1, 3, 4-oxathiazol-2-one. [b]Ref 5(a). [c]Absorption intensities; *m*(medium), (strong), and *vs*(very strong).

similar rearrangement mechanism described earlier. The same procedure but in ethyl ether resulted in the formation of 4-bromobenzonitrile(80 %). The formation of 4-boromobenzonitrile in ethyl ether can be ex-



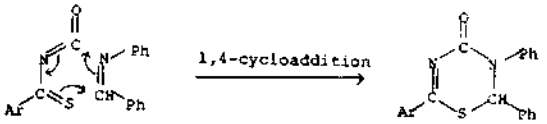
plained by fragmentation[5(a)] of thioacyl isocyanate to nitrile. And intermolecular 1, 4-cycloaddition of thioacyl isocyanate to nitrile can be considered as alternative mechanism.



6 d

But there is something questionable in this mechanism because **d** was not detected during the reaction.

The reaction of 4-bromothiobenzoyl isocyanate with benzalaniline resulted in the formation



6 (Ar=4-BrPh) 7

of a new compound, 6-(4-bromophenyl)-2, 3-dihydro-2, 3-diphenyl-4H-1, 3, 5-thiadiazin-4-one by 1, 4-cycloaddition.

CONCLUSION

5-Aryl-1, 3, 4-oxathiazol-2-one underwent desulfurization reaction by triethylphosphite at 100~110°C for about 24 hours under nitrogen to give benzonitriles, ethyl phosphorothioate, and carbon dioxide in 66~94 %. And 5-(4-nitrophenyl)-1, 3, 4-oxathiazol-2-one was reacted with triethylphosphite(83 %), triphenylphosphite(0 %), triethylphosphine(93 %), and triphenylphosphine(98%) under similiar condition for desulfurization reaction. The plausible mechanism of the desulfurization reaction is the concerted intramolecular rearrangement after insertion of the trivalent phosphorus compound into the ring.

4-Bromothiobenzamide prepared from 4-bromobenzamide showed cyclization reaction with the chlorocarbonylsulfenyl chloride to give 5-(4-bromophenyl)-1, 2, 4-dithiazol-3-one in 85 % yield. The different cyclization mode between amide and thioamide with chlorocarbonylsulfenyl chloride was manifested by the differentiations in IR spectra. In chloroform, reaction of the dithiazolone with triphenylphosphite at 0°C under nitrogen resulted in the formation of thioacyl isocyanate (97 %), but in ehtyl ether, benzonitrile was produced (80 %) by the same procedure. This could be explained by fragmentation of the unstable thiocacyl isocyanate to benzonitrile. The 1, 4-cyclo-addition of the thioacyl isocyanate with benzalaniline gave 6-(4-bromophenyl)-2, 3-dihydro-2, 3-diphenyl-4H-1, 3, 5-thiadiazin-4-one in 23% yield.

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