HETEROCYCLES, Vol. 54, No. 1, 2001, pp. 237 - 248, Received, 1st May, 2000

THERMOLYSIS OF ETHOXYCARBONYL[2-PHENYL-2-(PHENYLSULFONYLHYDRAZONO)ETHYL]METHYLENETRIPHENYLPHOSPHORANES. FORMATION OF SUBSTITUTED PYRIDAZINONES

Suketaka Ito,* Akikazu Kakehi, Kyoko Okada[1], and Ikuko Shibazaki

Department of Industrial Chemistry, Faculty of Engineering,
Shinshu University, Wakasato, Nagano, 380-8553, Japan

Abstract — Ethoxycarbony[2-phenyl-2-(phenylsulfonylhydrazono)ethyl]-methylenetriphenylphosphoranes were prepared by the reaction of ethoxycarbonymethylenetriphenylphosphorane with phenylsulfonylhydrazones of phenacyl bromides. Thermolysis of the phosphoranes gave 6-phenyl-2-phenylsulfonyl-3(2*H*)-pyridazinones, 6-phenyl-4-phenylsulfonyl-3(2*H*)-pyridazinones, and 6-phenyl-2-phenylsulfonyl-4-triphenylphosphoranylidene-1,4-dihydro-3(2*H*)-pyridazinones, together with triphenylphosphine. The structure of disubstituted methylenetriphenylphosphorane was confirmed by an X-Ray diffraction method.

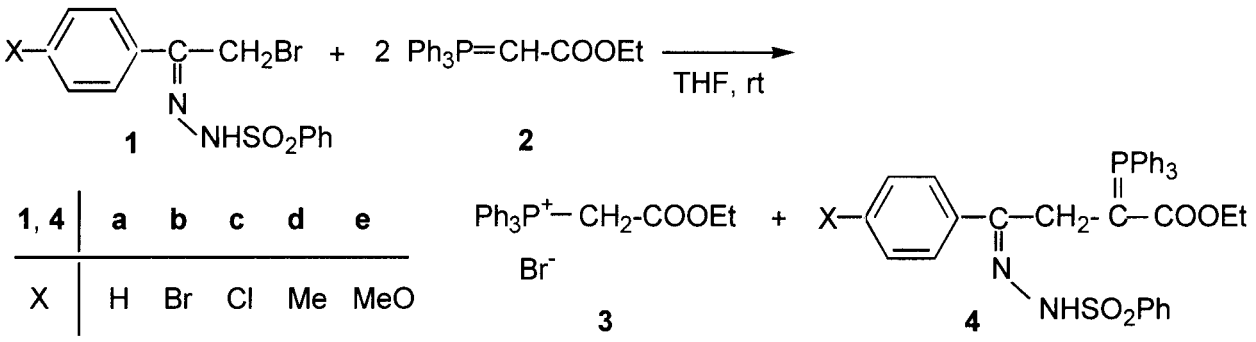
α-Halo ketone arylsulfonylhydrazones are known to undergo the base-induced 1,4-elimination of hydrogen halide giving arylsulfonylazoethylenes.[2] However, a stepwise reaction of the hydrazones, the substitution of α-halogen by suitable nucleophiles and the subsequent intramolecular process accompanying a release of arylsulfonyl group or alternative ones, may afford nitrogen-heterocycles.[3]

In a previous paper,[4] we reported the reaction of phenacylidenetriphenylphosphoranes[5] with phenylsulfonylhydrazones of phenacyl bromides to form 3,6-diphenylpyridazines and 5-benzoyl-3-phenylpyrazoles after thermolysis of the intermediate α-[2-phenyl-2-(phenylsulfonylhydrazono)ethyl]phenacylidenetriphenylphosphoranes. In the pyridazine formation, the liberation of triphenylphosphine oxide and benzenesulfinic acid was observed.

The present paper deals with the formation of 6-phenyl-2-phenylsulfonyl-3(2*H*)-pyridazinones, 6-phenyl-4-phenylsulfonyl-3(2*H*)-pyridazinones, and 6-phenyl-2-phenylsulfonyl-4-triphenylphosphoranylidene-1,4-dihydro-3(2*H*)-pyridazinones by thermolysis of ethoxycarbonyl[2-phenyl-2-(phenylsulfonylhydrazono)ethyl]methylenetriphenylphosphoranes prepared by the reaction of ethoxycarbonylmethylenetriphenylphosphorane with phenylsulfonylhydrazones of phenacyl bromides. In the thermolysis of phosphoranes, triphenylphosphine was recovered as a by-product.

Phenylsulfonylhyrazones (**1**), prepared from phenacyl bromides and phenylsulfonylhydrazine,[3] were allowed to react in THF with two molar amounts of ethoxycarbonylmethylenetriphenylphosphoranes (**2**) at room temperature; ethoxycarbonylmethyltriphenylphosphonium bromides (**3**) corresponding to **2** were formed almost quantitatively. After removal of the precipitated phosphonium salts by filtration, the THF solution was concentrated. To the concentrate, a portion of ethanol was added to give precipitates of ethoxycarbonyl[2-phenyl-2-(phenylsulfonylhydrazono)ethyl]methylenetriphenylphosphoranes (**4**) (Scheme 1), which were separated by filtration. The results are summarized in Tables 1 and 2.

In refluxing benzene, the phosphoranes (**4**) are comparatively stable and almost no reaction was observed; thus thermolysis was performed in dry toluene under reflux. After removal of the solvent from reaction mixtures, a portion of ethanol was added to the residue leading to separation into an ethanol-soluble and an ethanol-insoluble fraction. The ethanol-insoluble fraction was further treated with chloroform. Chromatographic treatment of the resulting chloroform-soluble fraction gave 6-phenyl-2-phenylsulfonyl-3(2*H*)-pyridazinones (**5**), 6-phenyl-4-phenylsul-fonyl-3(2*H*)-pyridazinones (**6**), and 6-phenyl-2-phenylsulfonyl-4-triphenylphosphoranylidene-1,4-dihydro-3(2*H*)-pyridazinones (**7**).



Scheme 1.

Table 1. Physical and Analytical Data of Methylenetriphenylphosphoranes (**4a**—**4e**)

Compd	Yield[a] (%)	Mp(decomp) (℃)	Formula	Found(Calcd)/% C	H	N
4a	69	175—176	$C_{36}H_{33}N_2O_4PS$	69.68(69.66)	5.38(5.35)	4.63(4.51)
4b	66	159—160	$C_{36}H_{32}N_2O_4BrPS$	61.52(61.80)	4.68(4.61)	4.10(4.00)
4c	66	174—175	$C_{36}H_{32}N_2O_4ClPS$	66.01(66.00)	4.95(4.92)	4.46(4.28)
4d	62	168—169	$C_{37}H_{35}N_2O_4PS$	70.15(70.01)	5.57(5.56)	4.45(4.41)
4e	55	139—140	$C_{37}H_{35}N_2O_5PS$	68.08(68.29)	5.30(5.42)	4.35(4.30)

a. Isolated Yield.

Table 2. Spectral Data of Phosphoranes (**4a**—**4e**)

Compd	IR(KBr, ν / cm^{-1})					^1H NMR($CDCl_3$, δ)[a]			
	NH	C=O	SO_2	Ph-P	Ph_3P^+-	CH_2[J_{PCCH}(Hz)]	CH_3CH_2-	CH_3CH_2-	NH
4a	2703	1566	1319, 1171	1437	1103	3.34d[16.6]	3.92q[b]	0.45t[c]	11.91br s
4b	2683	1566	1310, 1169	1439	1103	3.28d[16.6]	3.70q[b]	0.46t[c]	11.77br s
4c	2687	1570	1308, 1173	1439	1101	3.30d[16.6]	3.72q[b]	0.47t[c]	11.99br s
4d	2679	1558	1301, 1173	1439	1103	3.28d[16.6]	3.64q[b]	0.49t[c]	11.75br s
4e	2730	1599	1300, 1169	1439	1101	3.24d[16.6]	3.61q[b]	0.41t[c]	11.77br s

a. Multiplets near 7.0—8.0 ppm due to aromatic protons are omitted.
p-Me: **4d**, 2.20s. *p*-MeO: **4e**, 3.62s

b. *J*(Hz): 6.9.

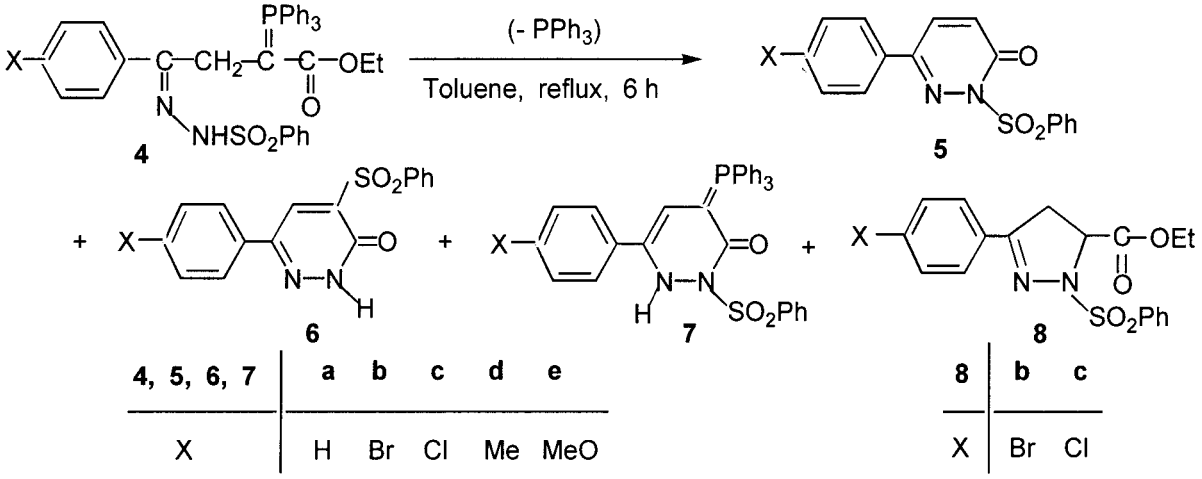
c. *J*(Hz): 7.2.

In addition, 5-ethoxycarbonyl-3-phenyl-1-phenylsulfonyl-4,5-dihydropyrazoles (**8**) were obtained also in the cases of **4b**,**c**. (Scheme 2.) In a similar manner, triphenylphosphine was recovered from the ethanol-soluble fraction. The results are listed in Tables 3 , 4 , and 5.

The chloroform-insoluble solid residue separated from the soluble fraction was a complex mixture of noncrystalline precipitates and undetermined.

The structure assignment of **4** was achieved on the basis of their analytical and spectral data, and the confirmation of **4a** was made also by an X-Ray diffraction method.

In the IR spectra of **4**, a broad band was found near 2700 cm^{-1} and a strong absorption near 1570 cm^{-1} assignable to ν CO. The ν CO-absorption peak of ethoxycarbonylmethylenetril-phenyphosphorane (**2**) could be seen at 1609 cm^{-1} (see: EXPERIMENTAL): the shift of ν CO-



Scheme 2.

Table 3. Physical and Analytical Data of 6-Phenyl-2-phenylsulfonyl- 3(2*H*)-pyridazinones (**5**), 6-Phenyl-4-phenylsulfony-3(2*H*)-pyridazinones (**6**), 6-Phenyl-2-phenylsulfonyl-4-triphenylphosphoranylidene-1,4-dihydro-3(2*H*)-pyridazinones (**7**), and 5-ethoxycarbonyl-3-phenyl-1-phenyl-sulfonyl-4,5-dihydropyrazoles (**8**)

Compd	Yield[a] (%)	mp[b] (℃)	Formula	Found(Calcd)/% C	H	N
5a	4	169—170[c]	$C_{16}H_{12}N_2O_3S$	61.53(61.53)	4.07(3.87)	8.77(8.97)
5b	4	181—182[d]	$C_{16}H_{11}N_2O_3BrS$	49.19(49.12)	2.69(2.83)	7.16(7.16)
5c	3	189—190[d]	$C_{16}H_{11}N_2O_3ClS$	55.31(55.42)	3.25(3.20)	8.19(8.08)
5d	8	187—188[d]	$C_{17}H_{14}N_2O_3S$	62.66(62.56)	4.40(4.32)	8.67(8.58)
5e	11	194—195[e]	$C_{17}H_{14}N_2O_4S$	59.70(59.64)	4.28(4.12)	8.34(8.18)
6a	10	296—297[c]	$C_{16}H_{12}N_2O_3S$	61.30(61.53)	3.83(3.87)	8.85(8.97)
6b	12	>300[c]	$C_{16}H_{11}N_2O_3BrSr$	49.11(49.12)	2.95(2.83)	7.35(7.16)
6c	16	>300[c]	$C_{16}H_{11}N_2O_3ClS$	55.45(55.42)	3.22(3.20)	8.14(8.08)
6d	3	294—295[e]	$C_{17}H_{14}N_2O_3S$	62.53(62.56)	4.31(4.32)	8.68(8.58)
6e	11	291—292[f]	$C_{17}H_{14}N_2O_4S$	59.58(59.64)	4.16(4.12)	8.10(8.18)
7a	20	197—198[g]	$C_{34}H_{27}N_2O_3PS$	71.03(71.07)	4.83(4.74)	4.88(4.87)
7b	17	194—195[g]	$C_{34}H_{26}N_2O_3BrPS$	62.27(62.49)	4.09(4.01)	4.37(4.29)
7c	13	202—203[g]	$C_{34}H_{26}N_2O_3ClPS$	66.87(67.05)	4.25(4.30)	4.74(4.60)
7d	14	216—217[g]	$C_{35}H_{29}N_2O_3PS$	71.29(71.41)	4.94(4.97)	4.71(4.76)
7e	14	194—195[g]	$C_{35}H_{29}N_2O_4PS$	69.70(69.52)	4.62(4.83)	4.43(4.63)
8b	18	177—178[c]	$C_{18}H_{17}N_2O_4BrS$	49.20(49.44)	3.84(3.92)	6.48(6.41)
8c	13	162—163[c]	$C_{18}H_{17}N_2O_4ClS$	54.73(55.03)	4.25(4.36)	7.29(7.13)

a. Isolated yield.
b. Componds (**7a**—**e**) were recrystallized from dichloromethane and the others from chloroform.
c. Colorless needles.
d. Colorless leaflets.
e. Pale yellow needles.
f. Yellow needles.
g. Orange prisms.

Table 4. Spectral Data of 3(2*H*)-Pyridazinones (**5**, **6**) and Dihydro-3(2*H*)-pyridazinones (**7**)

Compd	IR(KBr, ν / cm^{-1})					^{1}H NMR(DMSO-d_6, δ)[a]		
	NH	C=O	SO_2	Ph-P	Ph_3P^+-	4-H[$J_{4\text{-}5}$, Hz]	5-H[J_{PCCH}, Hz]	NH
5a		1688	1383, 1192			7.20d[10.2]	—[b]	
5b		1698	1381, 1192			7.23d[9.6]	—[b]	
5c		1698	1381, 1192			7.21d[9.8]	—[b]	
5d		1690	1383, 1194			7.15d[7.8]	—[b]	
5e		1690	1379, 1186			—[b]	—[b]	
6a	2866[d]	1657	1317, 1161				8.43s	13.71br s
6b	2870[d]	1657	1323, 1159				8.42s	13.72br s
6c	2874[d]	1657	1321, 1161				8.53s	13.86br s
6d	2888[d]	1663	1316, 1157				8.39s	13.57br s
6e	2890[d]	1661	1312, 1155				8.46s	13.69br s
7a	3437	1593	1341, 1163	1439	1109		5.13d[4.5]	—[c]
7b	3435	1588	1346, 1163	1439	1109		5.27d[4.2]	—[c]
7c	3422	1591	1345, 1165	1439	1109		5.34d[4.7]	—[c]
7d	3434	1591	1337, 1163	1437	1109		5.10d[4.0]	—[c]
7e	3428	1589	1343, 1163	1439	1109		5.20d[3.8]	—[c]

a. Multiplets near 7.0—8.5 ppm due to aromatic protons are ommited.
p-Me: **5d**, 2.34s; **6d**, 2.31s; **7d**, 2.17s. *p*-MeO: **5e**, 3.94s; **6e**, 3.73s; **7e**, 3.36s.

b. The proton signal is concealed by that of aromatic protons.

c. The signal assignable to an NH proton could not be confirmed. It is probably concealed by the proton signal of trace amounts of water in DMSO-d_6.

d. The strongest maximum of a broad complex absorption band is shown.

Table 5. Spectral Data of 4,5-Dihydrolpyrazoles (**8**)

Compd	IR(KBr, ν / cm^{-1})		^{1}H NMR($CDCl_3$, δ)[a]			
	C=O	SO_2	>CH-[*J*, Hz]	-CH_2-[*J*, Hz]	$CH_3C\underline{H}_2$-	$C\underline{H}_3CH_2$-
8b	1738	1370, 1165	4.49t[11.2]	3.34d[10.3]	4.30q[b]	1.36t[c]
8c	1738	1368, 1165	4.44t[11.2]	3.26d[10.3]	4.30q[b]	1.33t[c]

a. Multiplets near 7—8 ppm due to aromatic protons are omitted.

b. *J*(Hz): 6.9.

c. *J*(Hz): 7.2.

absorption (from 1609 to 1570 cm^{-1}) observed in **4** should be due to intramolecular hydrogen bonding. Thus, the broad band near 2700 cm^{-1} may be attributed to the NH-stretching vibration of amino group which is linked to the carbonyl oxygen by a hydrogen bond. Other characteristic absorption bands, ν Ph-P, asym. ν SO_2, sym. ν SO_2, and that owing to Ph_3P^+-, were found near 1440, 1310, 1170, and 1100 cm^{-1} respectively[6] (Table 2).

In the ^1H NMR spectra of **4**, the methylene- and the methyl-proton signals of ethoxy group were observed near δ = 3.7 and near δ = 0.5, respectively; these signals of ethoxycarbonylmethylenetriphenylphosphorane (**2**) were seen at δ = 4.05 and δ = 1.05. The unusual upfield shift of methyl-proton signal and that of methylene-proton signal should be due to the large shielding effect of the phosphoranylidenobenzene ring faced to the ethoxy group. In view of the intramolecular hydrogen bond presumed on the basis of IR spectra and the upfield shift of methyl-proton signal in NMR spectra, the hydrazono moieties of compounds (**4**) should be in an *E* configuration and the P=C and the C=O bond in an *s-trans* manner (Figure 1).

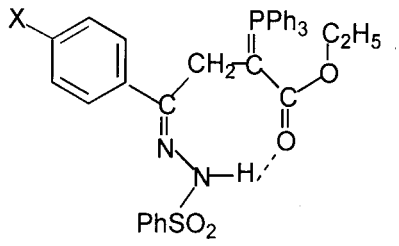


Figure 1. Configuration of **4**

The X-Ray analysis established the structure of **4a** unambiguously as ethoxycarbonyl[2-phenyl-2-(phenylsulfonylhydrazono)ethyl]methylenetriphenylphosphorane. A single crystal of **4a** was obtained as an almost colorless prism without further recrystallization. The ORTEP drawing for **4a** is shown in Figure 2.

The observed nitrogen-hydrogen bond length in the sulfonylhydrazono group (N2—H1) is 0.87 Å, which is shorter than that observed in α-[2-phenyl-2-(phenylsulfonylhydrazono)ethyl]phenacylidenetriphenylphosphorane (1.243 Å).[4] This fact implies the intramolecular hydrogen bonding between the amino hydrogen and the carbonyl oxygen in compound (**4a**) to be weak.

The structure of products (**5**, **6**, **7**, and **8**) was assigned also by analytical and spectral means. As shown in Tables 4 and 5, all compounds exhibit characteristic ν CO- and ν SO_2-absorption bands in their IR spectra. The broad complex band near 2880 cm^{-1} observed in the IR spectra of **6** may be attributed to ν NH-absorption owing to hydrogen bonding. This hydrogen bond may suggest the same type of bimolecular association that observed in 2-pyridone.[7] The MS spectrum of **5a** (ionization energy: 70 eV) has the $M^{+\cdot}$ ion peak (m/z 312, 48.1%) along with the following fragment ion peaks: m/z 248 (99.5%), 247 (99.5), 220 (100), 191 (6.4), 171 (8.4), 145 (10), 141 (30), 115 (100), 103 (13.7), 102 (37), 77 (99.5), 51 (99.5), and other minor ion peaks. This MS spectrum leads to the 6-phenyl-2-phenylsulfonyl-3(2*H*)-pyridazinone structure.

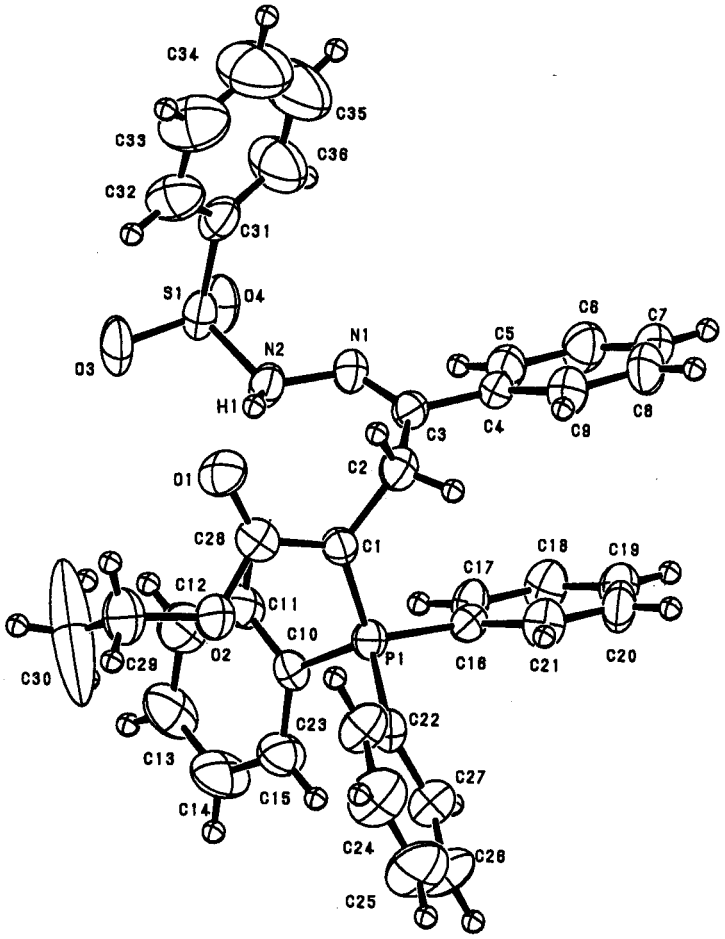


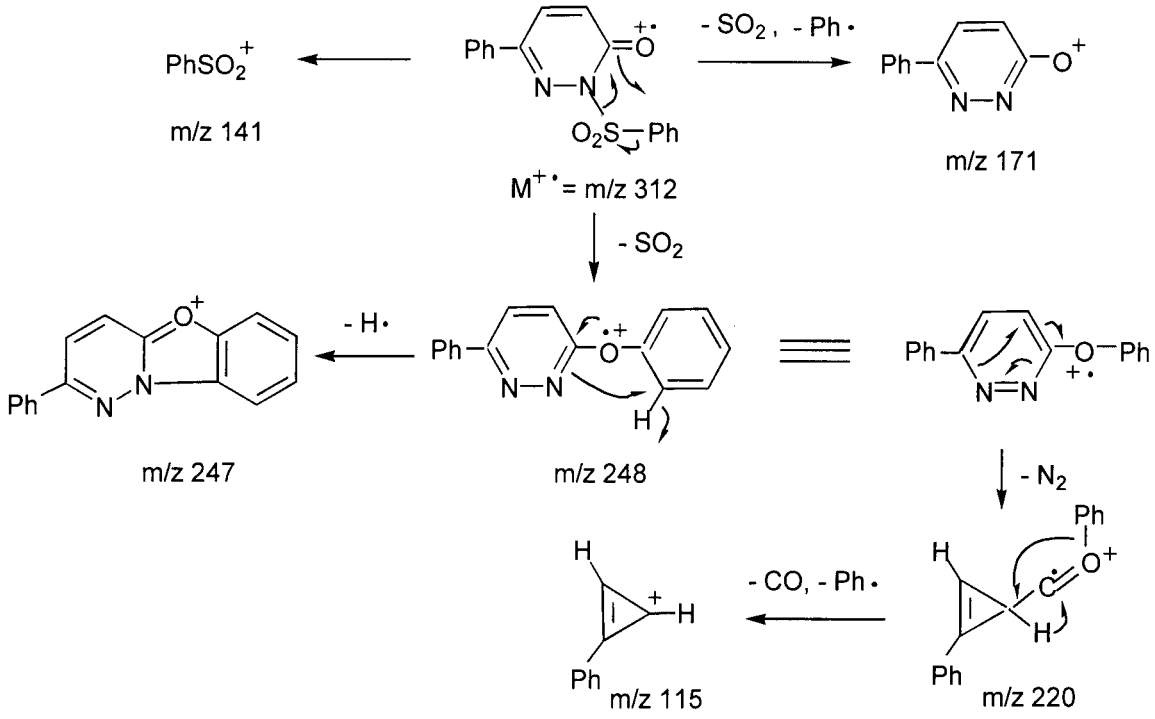
Figure 2. X-Ray Crystallographic Structure of **4a**[9]

A reasonable route to the main fragment ions is shown in Scheme 3.

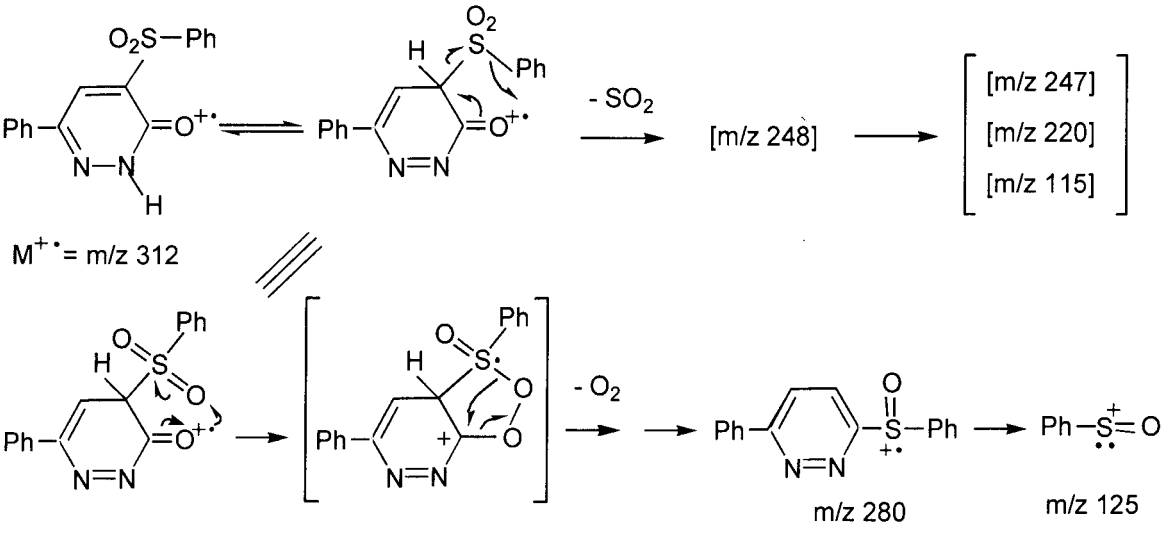
Compound (**6a**) gave an MS spectrum similar to that of **5a** which differs from that of **5a** only in absence of m/z 141 and presence of m/z 280 and 125 ion peaks. The significant ion peaks in the MS spectrum of **6a** are as follows: m/z 312 ($M^{+\cdot}$, 26.9%), 280 (9.6), 248 (100), 247 (98.7), 220 (19.7), 191 (26.5), 171 (13.2), 145 (22), 125 (40), 115 (98.8), 103 (20.9), 102 (30.9), 77 (97.7), 51 (97.7). Therefore, this MS fragmentation should lead to the 6-phenyl-4-phenylsulfonyl-3(2*H*)-pyridazinone structure (Scheme 4).

Because of thermal decomposition in the ionization chamber of mass spectrometer, no reasonable MS spectrum could be obtained from compound (**7a**). However, compounds (**7**) are characteristic of β-ketophosphorane in their IR spectra similarly to those of compounds (**4**). In addition, the IR absorption near 3400 cm^{-1} can be assigned to ν NH of anino group, which suggests the absence of hydrogen bonding such as in compounds (**6**). The NMR spectra of **7** exhibit the presence of one vinyl proton which is subjected to the spin-spin interaction with phosphorous. A cyclic structure for **7** is supported by the microanalysis; thus, compounds (**7**) may be reasonably assigned to 6-phenyl-2-phenylsulfonyl-4-triphenylphosphoranylidene-1,4-dihydro-3(2*H*)-pyridazinones.

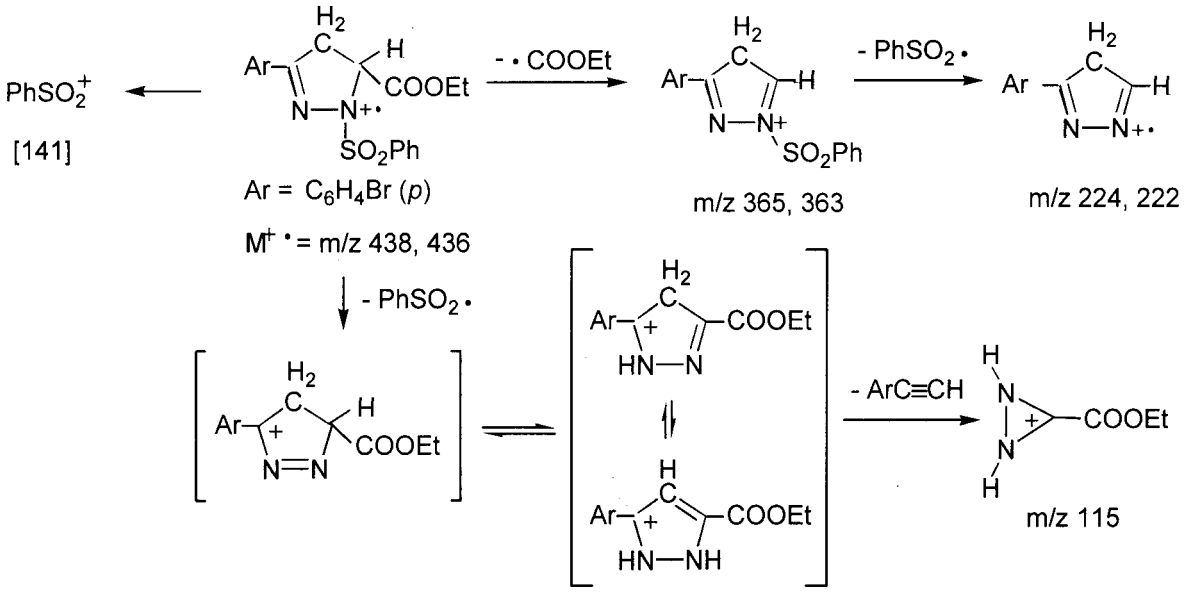
The MS spectrum of **8b** exhibits the $M^{+\cdot}$ ion peak (m/z 438, 17.9%; m/z 436, 17.5%) along with the following fragment ion peaks: m/z 365(37.3%), 363 (38.4), 296 (1.1), 294 (1.1), 269 (2.3), 267 (2.3), 241 (4.3), 239 (5.3), 224 (6.3), 222 (5.3), 213 (6.3), 211 (6.3), 197 (1.3), 196 (3.4), 195 (8.4), 194 (2.3), 193 (7.4), 185 (4.2), 183 (4.2), 141 (56.5), 115 (38.4), 77 (100), and other minor ion peaks. Thus, this MS fragmentation results in the assignment to 5-ethoxycarbonyl-3-(*p*-bromophenyl)-1-phenylsulfonyl-4,5-dihydropyrazole. A reasonable route to the main fragment ions is shown in Scheme 5.



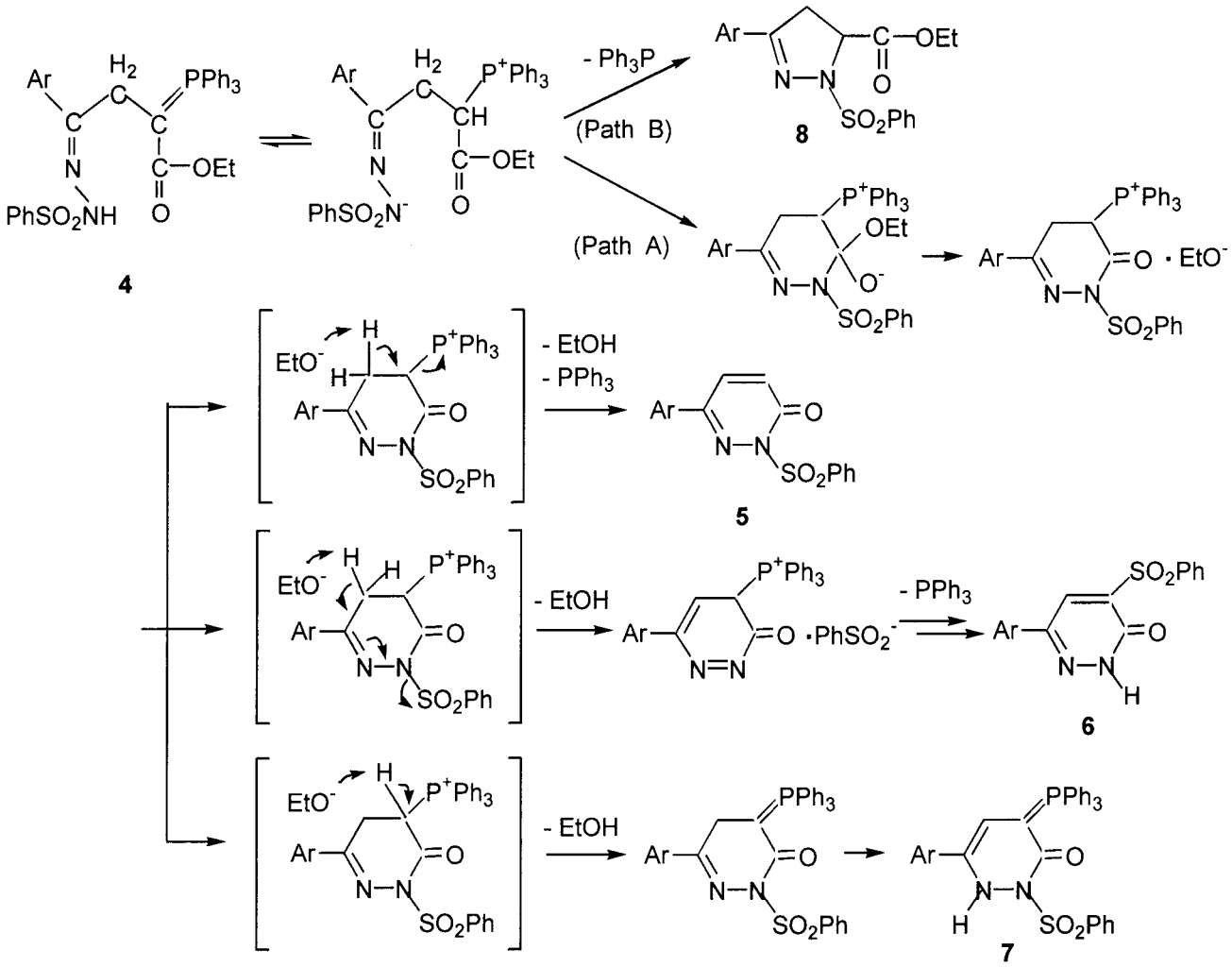
Scheme 3.



Scheme 4.



Scheme 5.



Scheme 6.

The formation of **5**, **6**, **7**, and **8** from **4** can be reasonably interpreted by considering intermediacy of phosphonium betaines regenerated from **4**. (Scheme 6.)

In the betaine form, the intramolecular nucleophilic process (nucleophilic addition) of hydrazonide nitrogen to the carbonyl carbon results in the formation of a six-membered ring, a phosphonioalkoxide (Path A), from which 4-triphenylphosphoranylidene-1,4-dihydro-3(2*H*)-pyridazinones (**7**) are generated *via* the elimination of ethanol followed by a prototropy in the pyridazinone ring. From the same intermediate (phosphonioalkoxide), pyridazinones (**5** and **6**) should be formed *via* the course indicated in Scheme 6.

Another intramolecular nucleophilic process (substitution) by the hydrazonide nitrogen may cause release of triphenylphosphine directly from the phosphonium betaine to afford dihydropyrazoles (**8**) (Path B). According to the HSAB principle, carbonyl carbon centers are hard acids, whereas saturated carbon centers as acids (for example, in nucleophilic substitutions) are soft. Therefore, the hydrazonide nitrogen (a hard base) of betaine should combine to the ester carbonyl leading to the formation of pyridazinones. On the other hand, the hardness of hydrazonide nitrogen may be reduced by the electron withdrawing *p*-bromo or *p*-chloro substituent on phenyl group; thus, in the cases of **4b**,**c**, the formation of dihydropyrazoles proceeds in competition with that of pyridazinones.

EXPERIMENTAL

Melting points were measured with a Yanaco MP-J3 micromelting point apparatus and are uncorrected. The microanalysis was done on a Perkin-Elmer 240 elemental analyzer. The IR, NMR, and MS spectra were recorded with a JASCO FT/IR-5800s spectrophotoeter, a Hitachi R-600 spectrometer (60 MHz), and a Hitachi M-80B mass spectrometer, respectively.

Phenylsulfonylhydrazones (**1**) of phenacyl bromides were obtained by the method previously reported.[3] Ethoxycarbonylmethylenetriphenylphosphorane (**2**) was prepared according to the method described in the literature,[8] mp 124—125 ℃ (lit.,[8] mp 125 —127.5 ℃). IR(KBr, cm^{-1}): 1609 (υ CO), 1437 (υ Ph-P), 1105 (υ Ph_3P^+-). ^{1}H NMR($CDCl_3$, δ) : 4.05q [*J*=6.4 Hz] ($CH_3C\underline{H}_2$-), 2.91 br s (>CH-), 1.05t [*J*=7.0 Hz] ($C\underline{H}_3CH_2$-).

Reaction of Phenylsulfonylhydrazones (1) of Phenacyl Bromides with Ethoxycarbonylmethylenetriphenylphosphorane (2). General Procedure: A solution of **2** (10 mmol) in THF (20 mL) was added dropwise to a solution of **1** (5 mmol) in THF (10 mL) and the reaction mixture was allowed to stand overnight. After removal of ethoxycarbonylmethyltriphenylphosphonium bromide (**3**) that precipitated by filtration (yields: almost quantitative), the filtrate was concentrated and then a 30-mL portion of ethanol was added to the concentrate. The separated crystalline product (almost colorless columns), ethoxycarbonyl[2-phenyl-2-(phenylsulfonylhydrazono)ethyl]methylenetriphenylphosphorane (**4**) was collected by filtration and washed with ethanol. The results are summarized in Tables 1 and 2. The products were in a fairly or almost pure state and further purification was not required.

Thermolysis of Ethoxycarbonyl[2-phenyl-2-(phenylsulfonylhydrazono)ethyl]methylene-triphenylphosphoranes (4). **Typical Procedure**: A 5-mmol portion of phosphorane (**4a**) (3.10 g) was heated for 6 h in dry toluene (150 mL) under reflux. After removal of solvent, a 30-mL portion of ethanol was added to the residue. The ethanol-insoluble solid mass was separated and treated with chloroform (80 ml, 60℃). The hot chloroform-insoluble residual was a complex mixture of noncrystalline precipitates (*ca.* 1 g) and undetermined.

The resulting chloroform solution was concentrated and chromatographed on a silica gel column (15 g, 2-cm d, 30-cm h; eluent: chloroform) to give pyridazinones (**5a**, 63 mg, 4%; **6a**, 156 mg, 10%; **7a**, 575 mg, 20%, respectively). These products were recrystallized from chloroform or dichloromethane (**7a**).

From the ethanol-soluble fraction, small amounts of triphenylphosphine were separated by a silica gel column chromatographic treatment (15 g, 2-cm d, 12-cm h; eluent: a hexane-benzene-ethanol system). In this treatment, an undeterminable oily mixture was also eluted..

Other phosphoranes (**4b**—**4e**) were treated in a similar manner. From **4b** and **4c**, 4,5-dihydropyrazoles (**8b** and **8c**) were obtained additionally. The results are shown in Tables 3, 4, and 5.

X-Ray Structural Determination of 4a:[9] Crystallographic data were collected on a Rigaku AFC5S diffractometer with graphite monochromated MoKα radiation (λ=0.71069 Å) using the ω-2θ (2θ max =50.0°) scan technique (4452 reflextions).

The crystal structure was solved by a direct method (MITHRIL, an integrated direct method computer program: C. J. Gilmore, *J. Appl. Cryst.*,1984, **17**, 42) and refined by a full-matrix least-squares procedure on $4F_O^2/\sigma^2(F_O^2)$, using 2335 reflextion [I >3.00 σ (I)] for 424 variables. The non-hydrogen atoms were refined anisotropically. The final R and Rw values are 0.045 and 0.051, respectively (max. shift/error, 0.53 $\Delta\rho_{max}$/e$^-$/Å^3, 0.28; $\Delta\rho_{min}$/e$^-$/Å^3, -0.28). (Computer program: TEXAN system, TEXAN—TEXRAY Structure Analysis Package, Molecular Structure Corporation, (1985)). Crystallographic details: $C_{36}H_{33}N_2O_4PS$, M = 620.70; monoclinic, space group, $P2_1/n$(Z=4); lattice parameter, a =10.147(5) Å, b =14.07(1) Å, c =12.964(6) Å, β =100.07(4)° , V/Å^3=3228(3). D_{calcd}=1.227 gcm^{-1}; crystal size, 0.580×0.660×0.980mm^3.

ACKNOWLEDGEMENT

The authors are grateful to Mrs. Teruko Tsuchida, Faculty of Engineering, Shinshu University, for the measurement of MS spectra.

REFERENCES

1. Present address: Kao Corporation, Research and Development Labolatories, 1334 Minato, Wakayama 640-8404 Japan.
2. G. Mossa and L.Caglioti, *J. Chem. Soc.* B, **1968**, 1404; L. Caglioti and G. Rosini, *Chem. Ind.* (London), **1969**, 1093.

3. S. Ito, A. Kakehi, and T. Miwa, *Heterocycles*, 1991, **32**, 2373; S .Ito, A. Kakehi, and A. Yamazaki, *Chem. Lett.*, **1990**, 453; S. Ito, A. Kakehi, K. Okada, S. Goto, and H. Kawaguchi, *Heterocycles*, 1997, **45**, 889.
4. S. Ito, A. Kakehi, and K. Okada, *Heterocycles*, 1999, **51**, 2949.
5. For a leading reference concerning to the chemistry of alkylidenephosphoranes, see: A. W. Johnson, "Ylides and Imines of Phosphorus," John Wiely & Sons, Inc., New York, 1993.
6. For references concerning to IR spectra of methylenephosphoranes, see: L. Horner and H. Oediger, *Liebigs Ann. Chem.*, 1959, **627**, 142; G. Aksnes, *Acta Chem. Scand.*, 1961, **15**, 692; A. J. Speziale and K. W. Ratts, *J. Org. Chem.*, 1963, **28**, 465.
7. H. Shindo, *Chem. and Pharm. Bull.*, **1959**, 7, 407.
8. D. B. Denney and S. T. Ross, *J. Org. Chem.*, 1962, **27**, 998.
9. Selected bond lengths (Å): S1-C31, 1.745(6); S1-N2, 1.632(4); N2-H1, 0.87(4); N2-N1, 1.394(5); N1-C3, 1.288(6); C3-C4, 1.493(6); C3-C2, 1.513(6); C2-C1, 1.519(6); C1-C28, 1.407(7); C28-O1, 1.246(5); C28-O2, 1.373(5); O2-C29, 1.449(6); C1-P1, 1.723(5); P1-C10, 1.819(5); P1-C16, 1.808(5); P1-C22, 1.811(5).
   Selected bond angles (°): C31-S1-N2, 106.1(2); S1-N2-H1, 116(3); S1-N2-N1,113.4(3); H1-N2-N1, 121(3); N2-N1-C3, 118.7(4); N1-C3-C2, 126.0(4); N1-C3-C4, 112.5(4); C2-C3-C4, 121.6(4); C3-C2-C1, 117.9(4); C2-C1-C28, 118.1(4); C1-C28-O1, 126.8(5); O1-C28-O2, 120.4(5); C28-O2-C29, 118.1(4); C2-C1-P1, 122.9(3); C28-C1-P1, 119.0(4); C1-P1-C10, 111.2(2); C1-P1-C16, 109.5(2); C1-P1-C22, 115.2(2); C10-P1-C16, 106.6(2); C10-P1-C22, 109.1(2); C16-P1-C22, 104.8(2).
   Tables of the coordinates, bond lengths, bond and torsion angles, and F_O-F_C tables have been deposited at the Cambridge Crystallographic Data Centre.