DEGRADATIONAL CYCLIZATION OF α-[2-PHENYL-2-(PHENYLSULFONYLHYDRAZONO)ETHYL]PHENACYLIDENETRIPHENYLPHOSPHORANES TO 3,6-DIPHENYLPYRIDAZINES AND 5-BENZOYL-3-PHENYLPYRAZOLES

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Abstract — α-[2-Phenyl-2-(phenylsulfonylhydrazono)ethyl]phenacylidenetriphenylphosphoranes were obtained (60−71%) by the reaction between phenylsulfonylhydrazones of phenacyl bromides and phenacylidenetriphenylphosphoranes. Thermolysis of the phosphoranes gave 3,6-diphenylpyridazines (43−66%) and 5-benzoyl-3-phenylpyrazoles (13−27%), together with triphenylphosphine oxide and *S*-phenyl benzenethiosulfonate, a disproportionation product from benzenesulfinic acid. The structure of the intermediate α-substituted phenacylidenetriphenylphosphorane was confirmed by an X-Ray diffraction method.

α-Halo ketone arylsulfonylhydrazones bearing a nucleophilic and an electrophilic center are utilizable bifunctional reactants. A stepwise reaction of the hydrazones, the substitution of α-halogen by suitable nucleophiles and the subsequent intramolecular process of the intermediates, may give nitrogen-heterocycles.[2]

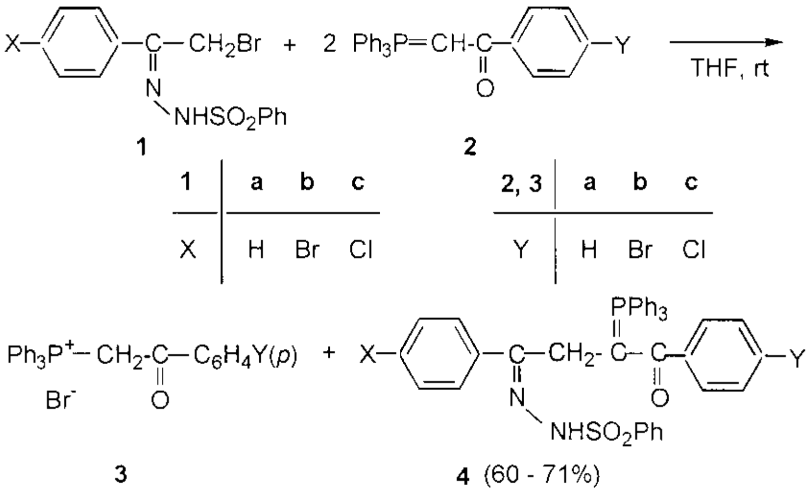
In a previous paper,[3] we reported that the reaction of phenacyl bromide phenylsulfonylhydrazone with quinoline and isoquinoline gives 2-phenylimidazoquinoline and -isoquinoline, respectively, with the release of benzenesulfonamide.

Analogously, 4-phenyl-1*H*-1,2,3-triazoles and 6-phenyl-3,4-diphenyl-2-phenylsulfonyl-2,3,4,5-tetrahydro-1,2,4-triazines were obtained by the reaction of title hydrazones with sodium azide[4] and with benzylideneaniline.[5]

In the present paper, we describe the reaction of phenacylidenetriphenylphosphoranes (**2**) with phenylsulfonylhydrazones (**1**) of phenacyl bromides[6] to form 3,6-diphenylpyridazines (**5**) and 5-benzoyl-3-phenylpyrazoles (**6**) after thermolysis of the intermediate α-[2-phenyl-2-(phenysulfonylhydrazono)ethyl]phenacylidenetriphenylphosphoranes (**4**).

Acyl- or aroylmethylenetriphenylphosphoranes react with azides,[7] nitrile imines,[8] and nitrile oxides[9] to give 1,2,3-triazoles, pyrazoles, and isoxazoles, respectively. The present work affords an alternative application of aroylmethylenetriphenylphosphoranes[10] for the synthesis of heterocycles.

Phenylsulfonylhyrazones (**1**), prepared from phenacyl bromides and phenylsulfonylhydrazine,[3] were allowed to react in THF with two molar amounts of phenacylidenephosphoranes (**2**) at room temperature. The precipitation of phenacyltriphenylphosphonium bromides (**3**) was observed. After removal of the precipitated phosphonium salts by filtration (yields: almost quantitative), the THF solution was concentrated. To the concentrate, a portion of benzene was added to give precipitates of α -[2-phenyl-2-(phenylsulfonylhydrazono)ethyl]phenacylidenetriphenylphosphoranes (**4**) (Scheme 1), which were separated by filtration. The results are summarized in Tables 1 and 2.



1 **2** **3** **4** (60 - 71%)

1	a	b	c
X	H	Br	Cl

2, 3	a	b	c
Y	H	Br	Cl

4	a	b	c	d	e	f	g	h	i
X	H	H	H	Br	Br	Br	Cl	Cl	Cl
Y	H	Br	Cl	H	Br	Cl	H	Br	Cl

Scheme 1.

Thermolysis of **4** was performed in dry benzene under reflux. Removal of the solvent from reaction mixtures followed by addition of ethanol brought about the separation of 3,6-diphenylpyridazines (**5**) as crystals, which were freed from the ethanolic solution by filtration.

Chromatographic treatment of the ethanol-soluble fraction gave 5-benzoyl-3-phenylpyrazoles (**6**) (Scheme 2) together with triphenylphosphine oxide and *S*-phenyl benzenethiosulfonate, one of the disproportionation products of benzenesulfinic acid.[11] The results are summarized in Tables 3, 4, and 5.

The structure assignment of **4**, **5**, and **6** was achieved on the basis of their analytical and spectral data; the confirmation of **4a** was made also by an X-Ray diffraction method. For direct comparison, compound (**5a**) was prepared by an alternative procedure.

Table 1. α-Substituted Phenacylidenetriphenylphosphoranes (**4a**—**4i**) Prepared by the Reaction of **1** with **2**

Compd	Yield[a] (%)	mp(decomp) (℃)	Formula	Found(Calcd)/% C	H	N
4a	71	150—151	$C_{40}H_{33}N_2O_3PS$	73.50(73.60)	5.00(5.09)	4.40(4.29)
4b	69	146—147	$C_{40}H_{32}N_2O_3BrPS$	65.61(65.67)	4.41(4.41)	4.03(3.83)
4c	62	154—156	$C_{40}H_{32}N_2O_3ClPS$	69.85(69.91)	4.65(4.63)	4.22(4.08)
4d	60	176—177	$C_{40}H_{32}N_2O_3BrPS$	65.62(65.67)	4.43(4.41)	3.90(3.93)
4e	63	137—138	$C_{40}H_{31}N_2O_3Br_2PS$	59.00(59.27)	4.00(3.85)	3.55(3.45)
4f	60	136—137	$C_{40}H_{31}N_2O_3BrClPS$	62.56(62.71)	4.13(4.07)	3.60(3.65)
4g	61	166—167	$C_{40}H_{32}N_2O_3ClPS$	69.78(69.91)	4.70(4.69)	4.16(4.08)
4h	69	131—132	$C_{40}H_{31}N_2O_3BrClPS$	62.41(62.71)	4.24(4.07)	3.77(3.65)
4i	67	134—136	$C_{40}H_{31}N_2O_3Cl_2PS$	66.53(66.57)	4.40(4.32)	3.85(3.88)

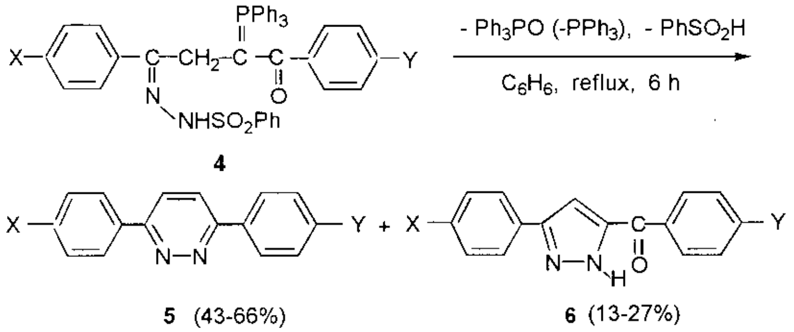
a. Isolated Yield.

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

Compd	IR(KBr, ν / cm^{-1})					^{1}H NMR(CDCl$_3$, δ)[a]		
	NH	C=O	SO_2	Ph-P	Ph_3P^+-	CH$_2$[J_{PCCH}(cps)][b]		NH
4a	2471	1410	1340, 1171	1437	1103	3.08d[20.3]	3.48d[14.8]	11.18br s
4b	2509	1410	1348, 1169	1437	1101	3.05d[20.1]	3.54d[15.9]	11.86br s
4c	2512	1414	1341, 1163	1437	1101	3.01d[20.2]	3.53d[15.7]	11.82br s
4d	3109	1503	1341, 1161	1439	1105	3.04d[19.7]	3.40d[14.2]	10.47br s
4e	2552	1412	1346, 1171	1437	1101	3.06d[20.9]	3.49d[15.7]	11.50br s
4f	2552	1412	1345, 1169	1437	1101	3.06d[20.5]	3.49d[15.0]	11.44br s
4g	3194	1503	1343, 1171	1439	1105	3.15d[18.5]	3.50d[14.6]	10.47br s
4h	2571	1414	1348, 1171	1437	1101	3.07d[20.5]	3.52d[15.2]	11.65br s
4i	2513	1410	1346, 1171	1437	1100	3.04d[20.2]	3.47d[15.5]	11.28br s

a. Multiplets near 7—8 ppm due to aromatic protons are ommited. Abbreviations are as follows: br s, broad singlet; d, doublet.

b. The areas of the downfield absorption relative to those of the upfield one (= 1.0) are as follows: **4a**, 1.0; **4b**, 0.79; **4c**, 0.87; **4d**, 3.2; **4e**, 2.7; **4f**, 3.9; **4g**, 4.7; **4h**, 3.1; **4i**, 3.2.



5, 6	a	b	c	d	e	f	g	h	i
X	H	H	H	Br	Br	Br	Cl	Cl	Cl
Y	H	Br	Cl	H	Br	Cl	H	Br	Cl

Scheme 2.

Table 3. 3,6-Diphenylpyridazines (**5a**—**5i**) Obtained from **4a**—**4i**

Compd	Yield[a] (%)	mp /℃ Found	mp /℃ Reported	Formula[b]	IR(KBr, ν /cm^{-1}) C=C	IR(KBr, ν /cm^{-1}) C=N
5a	61	226—227	222—223[c]	$C_{16}H_{12}N_2$	1487	1406
5b	61	246—247	238—239[d]	$C_{16}H_{11}N_2Br$	1487	1416
5c	61	237—238	228—229[d]	$C_{16}H_{11}N_2Cl$	1487	1418
5d	64	247—248	238—239[d]	$C_{16}H_{11}N_2Br$	1487	1416
5e	49	285—286	265—267[c]	$C_{16}H_{10}N_2Br_2$	1485	1420
5f	46	274—275		$C_{16}H_{10}N_2BrCl$	1485	1420
5g	66	237—238	228—229[d]	$C_{16}H_{11}N_2Cl$	1487	1418
5h	45	275—276		$C_{16}H_{10}N_2BrCl$	1485	1420
5i	43	267—268	265—267[c]	$C_{16}H_{10}N_2Cl_2$	1487	1420

a. Isolated Yield.

b. **5f**, Found(Calcd)/%: C, 55.36(55.60); H, 2.94(2.92); N, 7.84(8.11).
5h, Found(Calcd)/%: C, 55.68(55.60); H, 2.95(2.92); N, 8.22(8.11).
Satisfactory microanalyses (C, ±0.24; H, ±0.13; N, ±0.27%) were also obtained for all known compounds.

c. J. Nakayama, T. Tonishi, A. Ishii, and M. Hoshino, *Bull. Chem. Soc. Jpn.*, 1989, **62**, 2680.

d. Ref. 15.

Table 4. 5-Benzoyl-3-phenylpyrazoles (**6a**—**6i**) Obtained from **4a**—**4i**

Compd	Yield[a]	mp(decomp)	Formula	Found(Calcd)/%		
	(%)	(℃)		C	H	N
6a	13	174—175	$C_{16}H_{12}N_2O$	77.31(77.40)	4.84(4.87)	11.44(11.28)
6b	18	213—214	$C_{16}H_{11}N_2OBr$	58.53(58.74)	3.34(3.39)	8.48(8.56)
6c	15	221—222	$C_{16}H_{11}N_2OCl$	68.07(67.97)	3.89(3.92)	10.14(9.91)
6d	14	214—215	$C_{16}H_{11}N_2OBr$	58.51(58.74)	3.26(3.39)	8.68(8.56)
6e	27	230—231	$C_{16}H_{10}N_2OBr_2$	47.21(47.33)	2.41(2.48)	6.99(6.90)
6f	25	231—232	$C_{16}H_{10}N_2OBrCl$	52.91(53.14)	2.77(2.79)	7.47(7.55)
6g	16	208—209	$C_{16}H_{11}N_2OCl$	67.76(67.97)	3.80(3.92)	9.84(9.91)
6h	23	226—227	$C_{16}H_{10}N_2OBrCl$	53.10(53.14)	2.88(2.79)	7.98(7.75)
6i	24	222—223	$C_{16}H_{10}N_2OCl_2$	60.35(60.59)	3.15(3.18)	8.67(8.83)

a. Isolated Yield.

Table 5. Spectral Data of 5-Benzoyl-3-phenylpyrazoles (**6a**—**6i**)

Compd.	IR(KBr, ν / cm^{-1})			NMR(CDCl$_3$, δ)[a]
	NH	C=O	Pyrazole ring	NH
6a	3221	1636	1397, 1256	14.01bs
6b	3245	1634	1402, 1257	14.39bs
6c	3250	1642	1404, 1258	14.37bs
6d	3235	1626	1402, 1246	14.32bs
6e	3241	1630	1406, 1269	14.34bs
6f	3252	1622	1410, 1267	14.38bs
6g	3237	1626	1402, 1244	14.35bs
6h	3245	1634	1408, 1254	14.33bs
6i	3254	1622	1408, 1252	14.37bs

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

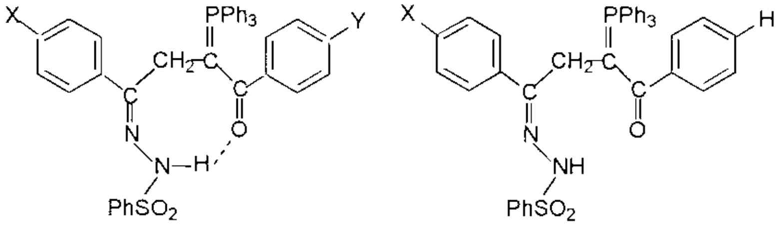
From the IR spectra of **4**, these compounds may be classified into two categories: in the IR spectra of **4a**,**b**,**c**,**e**,**f**,**h**,**i**, a broad band was found near 2500 cm^{-1} and a strong to medium peak near 1410 cm^{-1} assignable to ν CO.

The ν CO-absorption peak of phenacylidenetriphenylphosphorane (**2a**) can be seen at 1520 cm^{-1};[12] the shift of ν CO-absorption (from 1520 to 1410 cm^{-1}) observed in **4a**,**b**,**c**,**e**,**f**,**h**,**i** should be due to intramolecular hydrogen bonding. Thus, the broad band near 2500 cm^{-1} may be attributed to the NH-stretching vibration of amino group which is strongly linked to the carbonyl oxygen by a hydrogen bond.

On the other hand, the spectra of **4d**,**g** have a ν NH- and a ν CO-absorption peaks near 3200 and near 1500 cm^{-1}, respectively, which suggest the absence of intramolecular hydrogen bond to the carbonyl oxygen for these two compounds. In each member of **4**, other characteristic absorption bands, ν Ph-P, asym. ν SO$_2$, sym. ν SO$_2$, and that owing to Ph$_3$P$^+$-, were found near 1440, 1340, 1170, and 1100 cm^{-1} respectively.[13]

The spectral difference between **4d**,**g** and other members was found also in the ^{1}H NMR spectra: those of **4d**,**g** have a broad singlet owing to an NH proton near δ = 10.5, while those of other members in the range of δ = 11.2—11.9. This fact should reflect the absence or presence of intramolecular hydrogen bonding to the carbonyl oxygen for **4**. Two sets of doublet assignable to methylene protons were observed near δ = 3.1 and near δ = 3.5, which may be due to the presence of conformational isomers for the phosphoranes. The split of methylene proton signal into a doublet is attributable to the coupling with the P atom in a γ-position.

In view of the intramolecular hydrogen bond in compounds (**4a**,**b**,**c**,**e**,**f**,**h**,**i**), their hydrazono moieties should be in an *E* configuration and the P=C and the C=O bond in an *s-trans* manner; thus, these compound probably take an eight-membered, non-planar quasi-cyclic structure (Figure 1). The rotational barrier of triphenylphosphoranylidene group due to the pπ $-$dπ bond located in the P=C and the steric effect by the aryl group of Ar$-$C=O should result in the generation of two conformational isomers.



4a,b,c,e,f,h,i **4d,g**

Figure 1. Configuration of **4**

For **4d**,**g** lacking such intramolecular hydrogen bonding , the hydrazono moieties in a *Z* configuration might be conceivable. However, it is difficult to explain the absence of intramolecular hydrogen bonding on the basis of this type of isomerization, because **4d**,**g** are different from **4a**,**b**,**c**,**e**,**f**,**h**,**i** merely in their *p*-substituents (X and/or Y) in the two aryl groups. The hydrazono moieties of **4d**,**g** are probably also in an *E* configuration. For explaining this serious difference between **4a**,**b**,**c**,**e**,**f**,**h**,**i** and **4d**,**g**, we have assumed the resonance effect of the *p*-substituents. That is to say, the mesomeric effect of X in the β-hydrazonophenethyl groups would weaken the acidity of hydrazono hydrogen, while that of Y in the aroyl groups would strengthen the proton affinity of the carbonyl oxygen. In **4d**,**g**, only the proton-acidity weakening effect of X (X=Br, Cl) operates, from which the no formation of the hydrogen bonding results. The same situation as in **4a**,**b**,**c**,**e**,**f**,**h**,**i** is possible for the formation of two conformational isomers in **4d**,**g**.

The X-Ray analysis established the structure of **4a** unambiguously as α-[2-phenyl-2-(phenylsulfonylhydrazono)ethyl]phenacylidenetriphenylphosphorane. A single crystal of **4a**[14] was obtained as an almost colorless prism without further recrystallization. The PLUTO drawing for **4a** is shown in Figure 2.

The observed nitrogen-hydrogen bond length in the sulfonylhydrazono group (N1—H1) is 1.243 Å, which is longer than that in ordinary amines (~1.01 Å). This fact sugests strongly the intramolecular hydrogen bonding between the amino hydrogen and the carbonyl oxygen in **4a**. Furthermore, the acidity of the hydrazono hydrogen partly enhanced by the electron-withdraw-

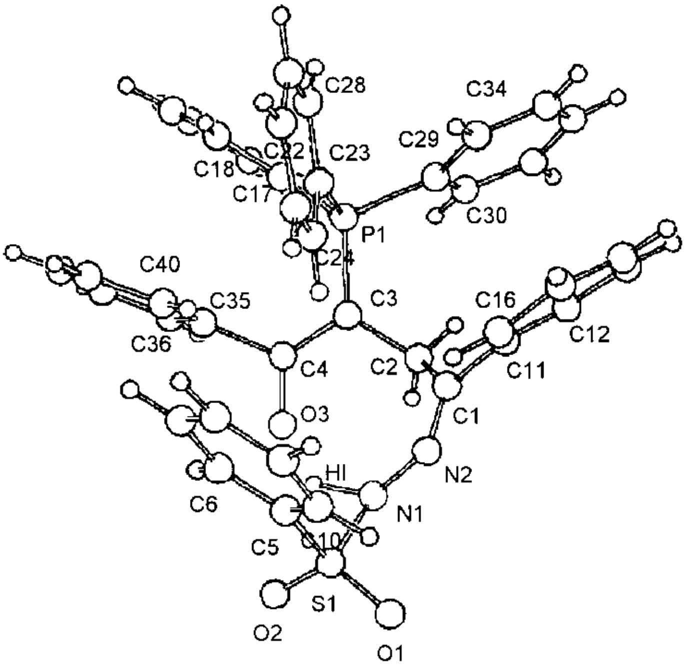


Figure 2. X-Ray Crystallographic Structure of **4a**[20]

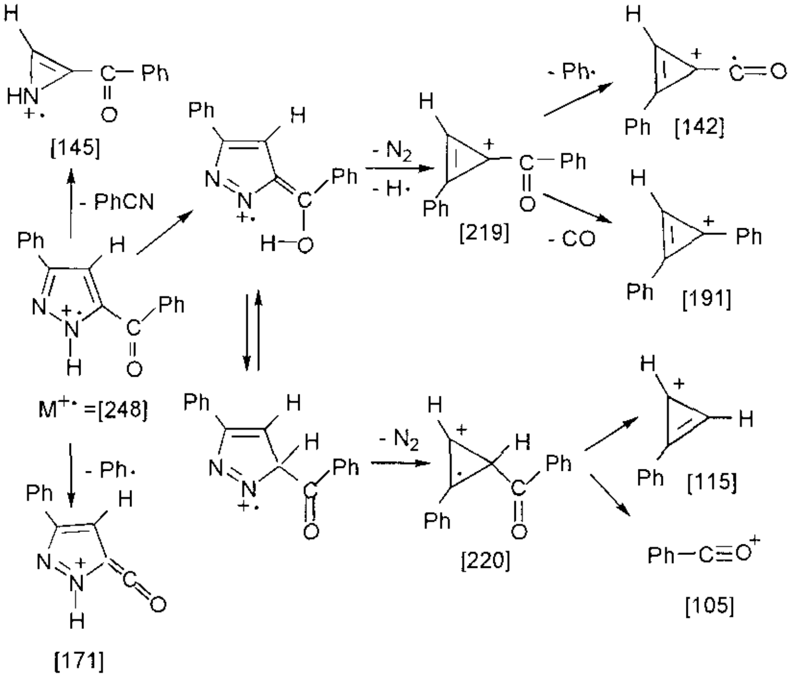
ing phenylsulfonyl group seems to contribute to the unusual nitrogen-hydrogen bond length.

The IR spectra of **5** have characteristic absorption bands of pyridazines near 1485 and near 1420 cm^{-1}, which have been assigned to ν C=C and C=N in pyridazine ring systems, respectively.[15] Compound (**5a**) was confirmed to be analytically and spectroscopically identical with 3,6-diphenylpyridazine which was prepared by an alternative procedure.[16]

In the IR spectra of **6**, the absorptions owing to ν NH and ν CO could be found near 3240 and near 1630 cm^{-1}, respectively. Two bands near 1400 and 1250 cm^{-1} are observed also in **6**, which can be assigned to the pyrazole-ring vibrations.[17] The ν NH-absorption of 3-benzoyl-5-phenypyrazole, the isomer of **6a**, has been reported to be 3356 cm^{-1} (dichloromethane),[18] while those of **6** are seen near 3200 cm^{-1}. In addition, no change was observed in the ν NH-absorption region of **6a** in a variety of concentration in chloroform (ν NH: 3216 cm^{-1}); thus, the shift of ν NH-absorption to a region of lower wave number suggests an intramolecular hydrogen bond in **6**.

The ^{1}H NMR spectra of **6** have a broad singlet due to an NH proton near δ = 14.3. The MS spectrum of **6a** (ionization energy: 70 eV) has the M$^{+\cdot}$ ion peak (m/z 248, 100%) along with the following fragment ion peaks: m/z 220 (12%), 219 (10), 191 (12), 171 (16), 145 (5.3), 142 (13), 115 (14), 105 (51), 77 (70), 51 (28), 43 (67), and other minor ion peaks, thus, this MS fragmentation should lead to the 5-benzoyl-3-phenylpyrazole structure (Scheme 3).

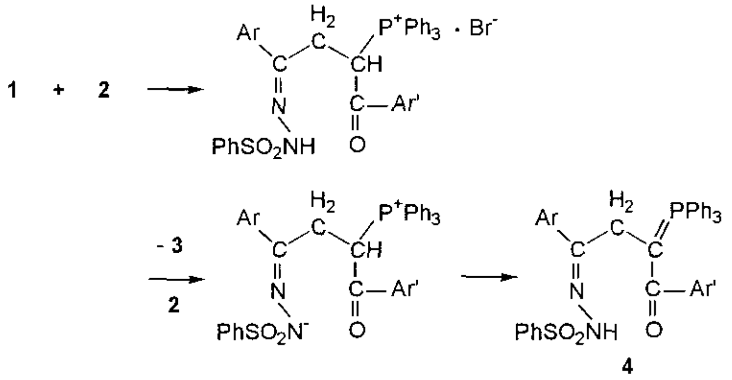
The reaction of phenacyl bromide with phenacylidenetriphenylphosphorane does not give α-phenacylphenacylidenetriphenylphosphorane but 1,2-dibenzoylethylene.[6] This product should



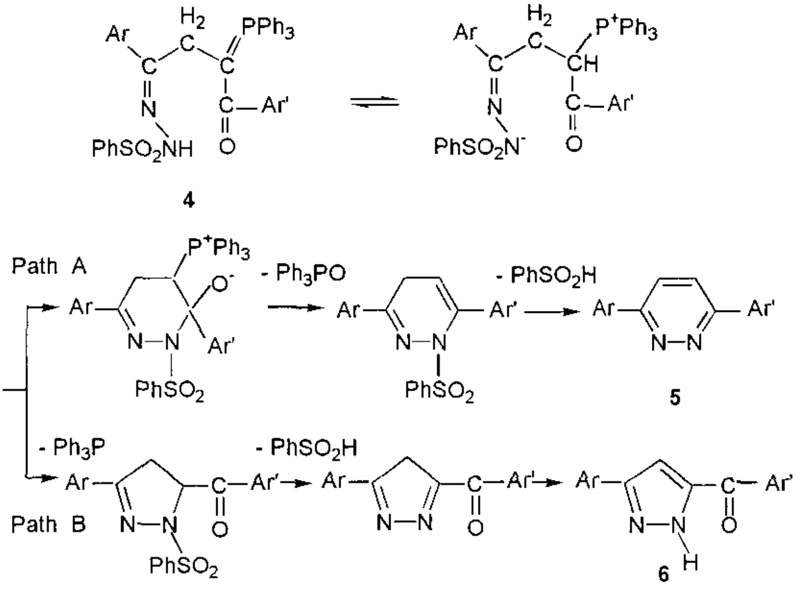
Scheme 3.

be formed *via* the β-elimination of a proton and triphenylphosphine from the intermediate (1,2-dibenzoyl)ethyltriphenylphosphonium ion by the action of phenacylidenetriphenylphosphorane as a base. However, as mentioned above, the reaction between phenylsulfonylhydrazones (**1**) of phenacyl bromides and phenacylidenetriphenylphosphoranes (**2**) does not proceed *via* such type of reaction course.

The difference of hydrazones (**1**) from phenacyl bromide in reactivity may be attributable to the acidity of the hydrazono hydrogen *in the intermediate* α-*[2-phenyl-2-(phenylsulfonylhydrazono)ethyl]*phenacyltriphenylphosphonium bromides. That is, the second molecule of **2** should abstract the acidic hydrazono hydrogen of intermediate phosphonium bromide in preference to methylene hydrogens. The resulting phosphonium betaine will isomerize to **4.** (Scheme 4.)



Scheme 4.



Scheme 5.

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

In the betaine form, intramolecular nucleophilic process (nucleophilic addition) of the hydrazonide nitrogen to the carbonyl carbon results in the formation of a six-membered ring, a phosphonioalkoxide, from which pyridazines (**5**) are generated *via* the elimination of triphenylphosphine oxide followed by that of benzenesulfinic acid (Path A). Another intramolecular nucleophilic course (substitution) by the hydrazonide nitrogen may cause release of triphenylphosphine from the phosphonium betaine and subsequent elimination of benzenesulfinic acid will afford pyrazoles (**6**) (Path B).

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 Varian EM-360A spectrometer, and a Hitachi M-80B mass spectrometer, respectively.

Phenylsulfonylhydrazones (**1**) of phenacyl bromides were obtained by the method previously reported,[3] and phenacylidenetriphenylphosphoranes (**2**) were prepared according to the method described in the literature.[19]

Reaction of Phenylsulfonylhydrazones (1) of Phenacyl Bromides with Phenacylidene-triphenylphosphoranes (2). General Procedure: A solution of **2** (8 mmol) in THF (20 mL) was added dropwise to a solution of **1** (4 mmol) in THF (10 mL) and the reaction mixture was allowed to stand overnight. After removal of phenacyltriphenylphosphonium bromide (**3**) that precipitated by filtration, the filtrate was concentrated and then a 30-mL portion of benzene was added to the concentrate. The separated crystalline product (almost colorless columns), α-[2-phenyl-2-(phenylsulfonylhydrazono)ethyl]phenacylidenetriphenylphosphorane (**4**) was collected by filtration and washed with benzene. 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 α-[2-Phenyl-2-(phenylsulfonylhydrazono)ethyl]phenacylidenetriphenylphosphoranes (4). Typical Procedure: A 3-mmol portion of phosphorane (**4a**) (1.96 g) was heated for 6 h in dry benzene (100 mL) under reflux. After removal of solvent, a 30-mL portion of ethanol was added to the resulting residue to separate pyridazine (**5a**) as crystals, which was collected by filtration and recrystallized from chloroform. The ethanol-soluble fraction was concentrated and chromatographed on a silica gel column (15 g, 2-cm d, 12-cm h; eluent: a hexane-benzene-ethanol system) to give pyrazole (**6a**) (98.3 mg, 13%) along with triphenylphosphine oxide and a small amount of *S*-phenyl benzenethiosulfonate (identified by means of IR-spectroscopy, respectively). Product (**6a**) was recrystallized from chloroform.

Other phosphoranes (**4b**—**4i**) were treated in a similar manner. The results are shown in Tables 3, 4, and 5.

X-Ray Structural Determination of 4a:[20] Crystallographic data were collected on a Rigaku

AFC5S diffractometer with graphite monochromated MoKα radiation (λ =0.71069 Å) using the ω-2θ (2θ max =55.0°) scan technique (4396 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 2161 reflextion [I >3.00σ (I)] for 424 variables. The non-hydrogen atoms were refined anisotropically. The final R and Rw values are 0.064 and 0.068, respectively (max shift/error, 0.73 $\Delta\rho_{max}$/e$^-$/Å^3, 0.90; $\Delta\rho_{min}$/e$^-$/Å^3, -3.84). (Computer program: TEXAN system, TEXAN—TEXRAY Structure Analysis Package, Molecular Structure Corporation, (1985)). Crystallographic details: $C_{40}H_{33}N_2O_3SP$, M = 652.75; orthorhombic, space group, $P2_12_12_1$(Z=4); lattice parameter, a =16.851(6) Å, b =17.685(2) Å, c =11.484(1) Å, $\alpha = \beta = \gamma$ =90° , V/Å^3=3423(1). D_{calcd}=1.267 gcm^{-1}; crystal size, 0.30×0.40×0.64 mm.

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17. Four medium-to-strong peaks at 1599, 1466, 1397, and 1256 cm^{-1} observed in the IR spectrum of 3,5-dimethylpyrazole have been assigned to pyrazole-ring vibrations, and the NH-absorption has been reported to be 3484 cm^{-1}: A. Zecchina, L. Cerruti, S. Coluccia, and E. Borello, *J. Chem. Soc.* B, **1967**, 1363.
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20. Selected bond lengths (Å): S1-C5, 1.769(9); S1-N1, 1.643(7); N1-H1, 1.243; N1-N2, 1.427(9); C1-N2, 1.31(1); C1-C2, 1.43(1); C1-C11, 1.49(1); C2-C3, 1.49(1); C3-P1, 1.758(7); C3-C4, 1.41(1); C4-O3, 1.26(1); C4-C35, 1.55(1): P1-C17, 1.803(8); P1-C23, 1.808(7); P1-C29, 1.828(8).

    Selected bond angles (°): C5-S1-N1, 104.9(4); S1-N1-H1, 91.86; S1-N1-N2,111.6(6); H1-N1-N2, 137.37; N1-N2-C1, 115.5(7); N2-C1-C2, 127.3(8); N2-C1-C11, 112.0(9); C2-C1-C11, 120.6(9); C1-C2-C3, 117.4(8); C2-C3-C4, 117.3(6); C2-C3-P1, 122.1(6); C4-C3-P1, 120.5(6); C3-C4-O3, 123.1(9); C3-C4-C35, 125.1(8); O3-C4-C35, 111.4(9); C3-P1-C17, 111.2(4); C3-P1-C23, 114.1(3);C3-P1-C29, 109.6(4); C17-P1-C23, 108.7(4); C17-P1-C29, 108.0(3); C23-P1-C29, 104.9(4).

    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.

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