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THE BEHAVIOUR OF α -DIKETONE MONO-, AND DI-IMINE SYSTEMS TOWARDS 2,4-BIS(PHENYLTHIO)-1,3-DITHIA-2,4-DIPHOSPHETANE-2,4-DISULFIDE (JAPANESE REAGENT, JR)

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THE BEHAVIOUR OF α -DIKETONE MONO-, AND DI-IMINE SYSTEMS TOWARDS 2,4-BIS(PHENYLTHIO)-1,3-DITHIA-2,4-DIPHOSPHETANE-2,4-DISULFIDE (JAPANESE REAGENT, JR)

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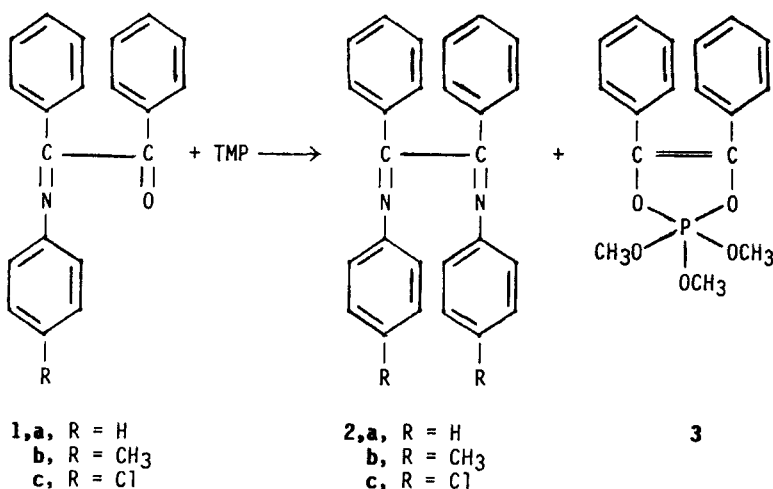
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2,4-Bis(phenylthio)-1,3-dithia-2,4-diphosphetane-2,4-disulfide (Japanese reagent, JR, 4) reacts with benzil monoanils **1a-c**, in boiling THF to give the respective 1,2-diphenyl-2-(phenylthio)-2-[arylamino]-ethane-1-thiones **6a-c**. Compound **6a** was also prepared by the action of $(P_2S_5)_x$ on **1a** followed by addition of thiophenol to the produced thione **5a**. Benzil dianils **2a-c** reacted with reagent 4 in dry toluene to yield the respective phenyl-(phenylthio)-[arylimino]-methane **8a-c**. Possible reaction mechanisms were considered and structures of the new products were supported by compatible analytical and spectroscopic evidences.

Key words: Benzil mono-imine; di-imines; Japanese reagent; homolytic fission, radical mechanism.

INTRODUCTION

Recently,¹ we have shown that, tertiary phosphite esters, namely trimethyl phosphite (TMP) induces the homolytic fission of the exocyclic carbon-carbon single bond in benzil monoanils **1a-c** to give the respective dianils **2a-c** and benzil. Intermediate formation of benzil was supported by isolation of its addition product with TMP, namely, 4,5-diphenyl-2,2,2-dimethoxy-1,3,2-dioxaphospholene **3**.^{2,3}

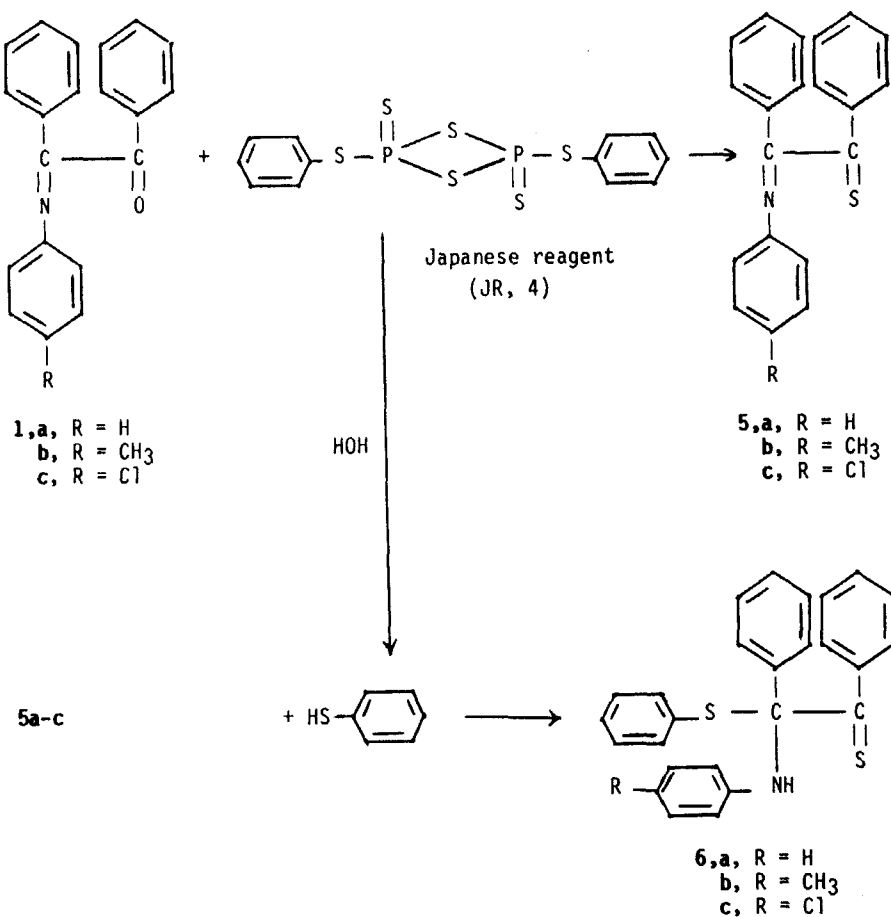


In response to our growing interest in the organophosphorus chemistry of α -diketone mono-, and di-imines^{1,4-7}, we have now studied the behaviour of benzil mono-, and dianils towards 2,4-bis(phenylthio)-1,3-dithia-2,4-diphosphetane-2,4-disulfide (Japanese reagent, JR, 4).

RESULTS AND DISCUSSION

We have found that the reaction of JR, 4, with benzil monoanils **1a-c** and benzil dianils **2a-c** proceeds smoothly in tetrahydrofuran and in dry toluene respectively under mild reaction conditions to give chromatographically pure products containing sulfur but no phosphorus (elemental analysis). These products were assigned structures **6a-c** and **8a-c**, respectively.

A mechanism that explains the formation of compounds **6a-c** is depicted in Scheme 1. This involves the initial conversion of monoanils **1a-c** to give the respective thiones **5a-c** under the thiating action of reagent **4**. Thiophenol (probably formed through hydrolysis of JR, 4, during the reaction course) adds to **5a-c** to give the final product **6a-c**.



[Scheme 1]

A support for this mechanism has been gained by the unequivocal synthesis of **6a** according to the following steps:

1. Action of phosphorus pentasulfide P_2S_5 on benzil monoanil **1a** to give the respective thione **5a**.

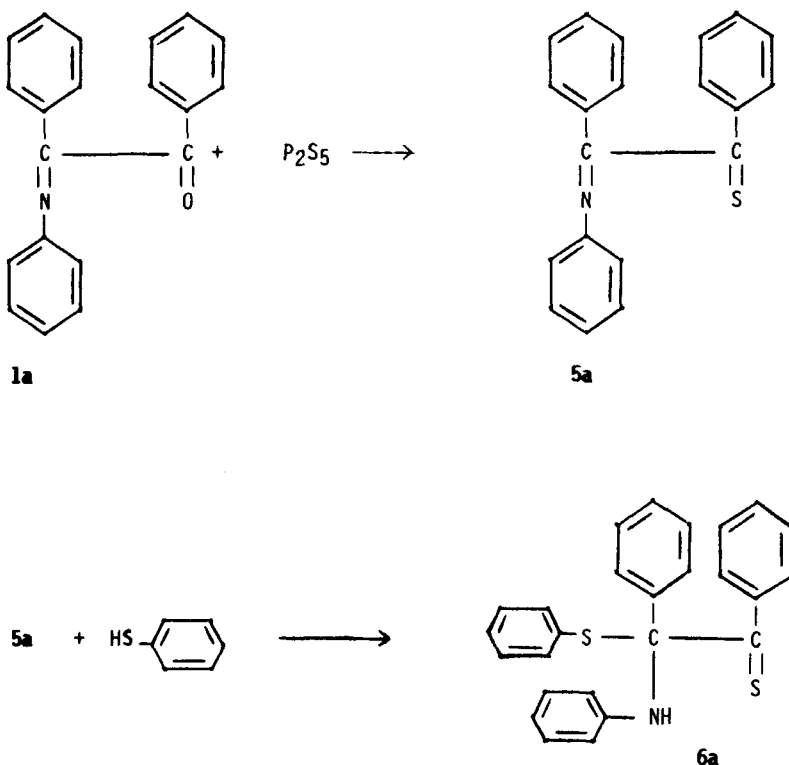
2. The reaction between the thione **5a** and thiophenol to give adduct **6a** [Scheme 2].

Apparently, the reaction of benzil monoanils **1a–c** with JR, **4**, can be interpreted in terms of radical reaction mechanism. The phenylthio radical formed during the radical reaction course can abstract a hydrogen radical (probably from moisture present in the medium) to give thiophenol which finally led to product **6a–c**.

The radical reaction mechanism is supported by the finding that no reaction proceeds between monoanil **1a** and JR, **4**, when a free radical inhibitor e.g. hydroquinone was added to the reactants.

The IR spectrum of the new products shows a strong absorption band of the $-\text{NH}$ group and the absence of the band of the carbonyl group.

Structural support for 1,2-diphenyl-2-(phenylthio)-2-[phenylamino]-ethane-1-thione **6a** taken as example was: [a] Its elemental analysis and molecular weight determination corresponded to $\text{C}_{26}\text{H}_{21}\text{NS}_2$ (m/z , 411), [b] Its IR spectrum lacked the $\text{C}=\text{O}$ group absorption which is recorded in the spectrum of anil **1a** at 1690 cm^{-1} . The spectrum, however, showed strong absorption bands in the region $1600\text{--}1500\text{ cm}^{-1}$ due to the aromatic $\text{C}=\text{C}$ stretching vibrations. The spectrum also, recorded

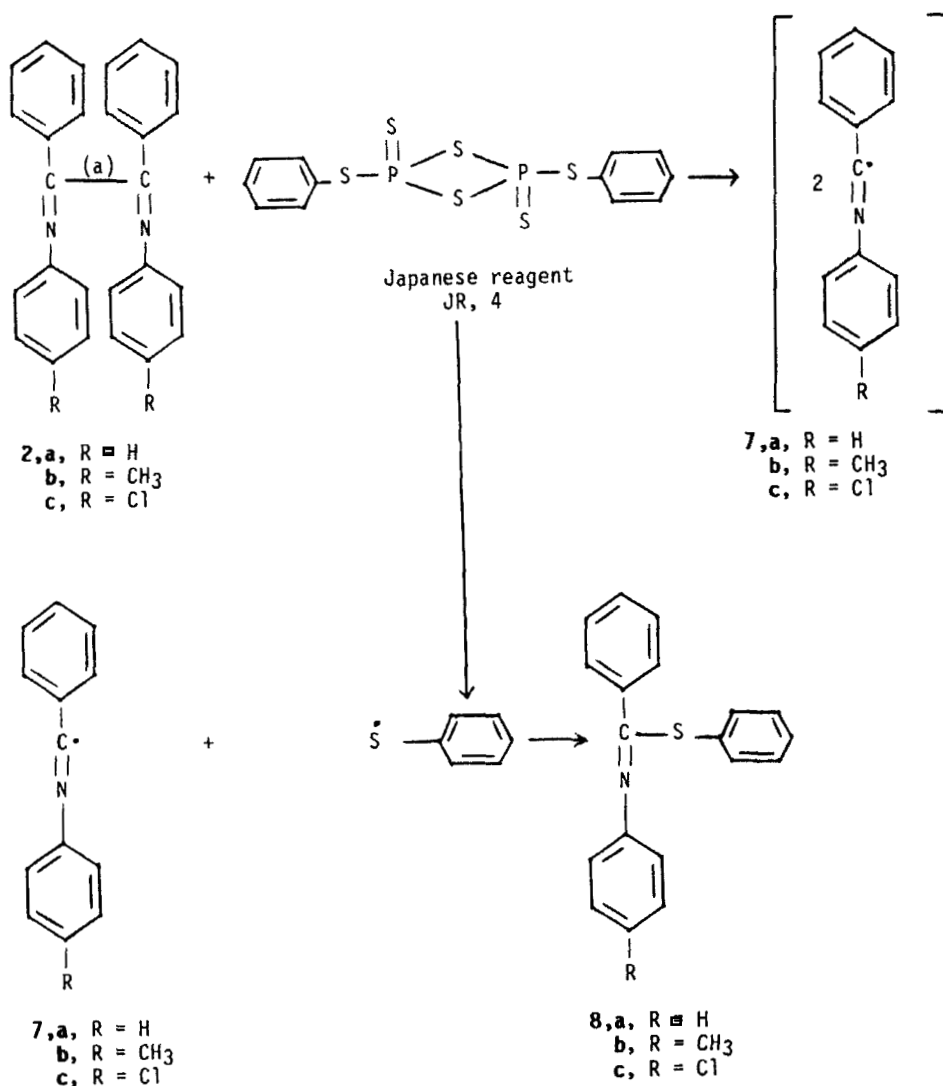


[Scheme 2]

a band at 1190 cm^{-1} due to the $\text{C}=\text{S}$. A strong band appeared at 3400 cm^{-1} due to the $-\text{NH}$ stretching vibrations.⁸ [c] The NMR spectrum of **6a** showed signals at δ 3.8 ppm (NH, broad singlet, exchangeable with D_2O) and the aromatic protons (20H) gave a multiplet in the δ 7.6–8 ppm region.⁹

Addition of JR, 4, to dianils **2a–c** proceeds in dry toluene to yield products **8a–c**.

A mechanism accounting for the formation of products **8a–c** depends on homolytic fission of the exocyclic carbon-carbon single bond of the dianil **2a–c** (along axis a) to yield radical species **7a–c**. Addition of phenylthio radical of the reagent 4, to radical **7a–c** yield products **8a–c** [Scheme 3].



[Scheme 3]

Addition of hydroquinone to the reaction medium of benzildianil **2a** and JR, **4**, prevents any reaction. This is in accord with the free radical mechanism of the reaction.

Structural support for phenyl-(phenylthio)-[phenylimino]-methane **8a** taken as example was: [a] Its elemental analysis and molecular weight determination corresponded to $C_{19}H_{15}NS$ (m/z, 289). [b] Its IR spectrum showed strong absorption

TABLE I
The physical and analytical data for compounds **6a-c**, **5a** and **8a-c**

Compound	Reaction conditions solvent/time	Solvent of crystallization	m.p. Yield		Formula M. wt	Analysis Calc./Found				
			°C	%		C	H	N	S	Cl
6a	THF/120 min.	Ethyl alcohol	162	68	$C_{26}H_{21}NS_2$ (411)	75.91	5.10	3.40	15.57	-
						75.80	4.98	3.20	15.25	-
6b	THF/90 min.	Benzene-pet.-ether	197	80	$C_{27}H_{23}NS_2$ (425)	76.23	5.41	3.29	15.05	-
						76.02	5.28	3.13	14.90	-
6c	THF/100 min.	Ethyl acetate	186	78	$C_{26}H_{20}NS_2Cl$ (445.5)	70.03	4.48	3.14	14.36	7.96
						69.85	4.33	3.01	14.17	7.75
5a	Toluene/120 min.	Ethyl alcohol	146	85	$C_{20}H_{15}NS$ (301)	79.73	4.98	4.65	10.63	-
						79.55	4.82	4.49	10.48	-
8a	Toluene/40 min.	Ethyl alcohol-ether	206	70	$C_{19}H_{15}NS$ (289)	78.89	5.19	4.84	11.07	-
						78.71	5.00	4.62	10.88	-
8b	Toluene/40 min.	Ethyl alcohol	189	83	$C_{20}H_{17}NS$ (303)	79.20	5.61	4.62	10.56	-
						78.97	5.40	4.47	10.35	-
8c	Toluene/50 min.	Ethyl alcohol-ether	224	76	$C_{19}H_{14}NSCl$ (323.5)	70.47	4.32	4.32	9.89	10.97
						70.33	4.18	4.20	9.72	10.82

TABLE II
The I.R. and 1H -NMR spectral data for compounds **6a-c**, **5a** and **8a-c**

Compound	I.R. cm^{-1}					1H -NMR ppm		
	C=S	C=N	C=C (aromatic)	CH ₃ -aryl	-NH	CH ₃	Aromatic	-NH
6a	1190	-	1500	-	3400	-	7.6-8.0(20H,m)	3.8(1H,s)
6b	1160	-	1540	2950	3410	2.2(3H,s)	7.5-8.1(19H,m)	3.6(1H,s)
6c	1180	-	1560	-	3395	-	7.5-8.0(19H,m)	3.9(1H,s)
5a	1190	1640	1510	-	-	-	7.5-8.2(15H,m)	-
8a	-	1640	1520	-	-	-	6.8-8.0(15H,m)	-
8b	-	1665	1510	2920	-	2.2(3H,s)	7.0-8.0(14H,m)	-
8c	-	1620	1560	-	-	-	7.2-8.1(14H,m)	-

bands in the region $1600\text{--}1500\text{ cm}^{-1}$ due to the aromatic $\text{C}=\text{C}$ stretching vibration. Also, a band at 1640 cm^{-1} appeared due to $\text{C}=\text{N}$ absorption band. [c] The NMR spectrum of **8a** showed a multiplet in the δ 6.8–8 ppm region due to aromatic protons (15 H). [d] The mass spectra showed a molecular ion peak at m/z 289, M^+ , 20%.

Table I summarizes the physical and analytical data of the new compounds.

Table II shows the spectral data of IR and ^1H -NMR.

CONCLUSION

It is evident that O/S exchange in the reactions of benzil monoanils **1a–c** with the Japanese reagent JR, 4, proceeds smoothly and quickly to give addition products **6a–c** in high percentage yields. Besides, the reaction of JR, 4, with benzil monoanils **1a–c** and benzil dianils **2a–c** can be considered as a simple and convenient route for the production of **6a–c** and **8a–c** in a one step reaction. Moreover, these findings explore new synthetic potentialities for the Japanese reagent.

EXPERIMENTAL

All melting points were uncorrected. Solvents were dried by standard techniques including high vacuum procedures. Benzil monoanils¹⁰ and benzil dianils¹¹ were freshly prepared and twice crystallized before use. Japanese reagent JR, 4, was prepared according to an established procedure¹² and twice recrystallized before use.

The IR spectra (run in KBr and expressed in cm^{-1}) were recorded with a Beckmann 4220 Infracord Model and the ^1H -NMR spectra were measured (in CDCl_3 or DMSO-d_6 and expressed in the δ -scale) at 60 MHz or 90 MHz on a Varian instrument using TMS as an internal standard. The mass spectra were performed at 70 eV using a Varian MAT 112 Mass spectrometer.

General procedure for the reaction of benzil monoanils 1a–c with Japanese reagent JR, 4. A mixture of 0.005 mol of benzil monoanils **1a–c** and 0.005 mol of reagent 4, was heated in 25 ml of tetrahydrofuran under reflux with stirring until no more of the starting materials could be detected (TLC). After removal of the volatile materials in vacuo, the residual substance was collected and recrystallized from the proper solvent to give:

- 1,2-Diphenyl-2-(phenylthio)-2-[phenylamino]-ethane-1-thione **6a**.
- 1,2-Diphenyl-2-(phenylthio)-2-[(4-methylphenyl)amino]-ethane-1-thione **6b**.
- 1,2-Diphenyl-2-(phenylthio)-2-[(4-chlorophenyl)amino]-ethane-1-thione **6c**.

Action of phosphorus pentasulfide (P_2S_5)_x on benzil monoanil 1a. A mixture of 0.005 mol of benzil monoanil **1a** and 0.005 mol of (P_2S_5)_x was heated in 25 ml of dry toluene under reflux with stirring for about 2 hr. After evaporation of the solvent, the solid material was collected and recrystallized from ethyl alcohol to yield thione **5a** m.p. 146°C .

The reaction between thione 5a and thiophenol. A mixture of 0.005 mol of thione **5a** and 0.005 mol of thiophenol was heated in 25 ml of tetrahydrofuran under reflux with stirring until no more of the starting material could be detected. After removal of the volatile material in vacuo, the solid material was collected and recrystallized from ethyl alcohol to give a product proved to be **6a** (m.p. mixed melting point and comparative IR spectra).

General procedure for the reaction of benzil dianils 2a–c with Japanese reagent JR, 4. A mixture of 0.005 mol of benzil dianils **2a–c** and 0.005 mol of reagent 4, was heated in 25 ml of dry toluene under reflux with stirring until no more of the starting materials could be detected (TLC). After removal of the volatile materials in vacuo, the residual substance was collected and recrystallized from the proper solvent to yield.

- Phenyl-(phenylthio)-[phenylimino]-methane **8a**.
- Phenyl-(phenylthio)-[(4-methylphenyl)-imino]-methane **8b**.
- Phenyl-(phenylthio)-[(4-chlorophenyl)-imino]-methane **8c**.

The reaction of benzil monoanil **1a** and/or benzil dianil **2a** with Japanese reagent JR, 4, in the presence of hydroquinone. A mixture of 0.005 mol of compound **1a** or **2a** and 0.005 mol of reagent 4 in presence of a few mgs of hydroquinone was heated in 25 ml of boiling solvent (THF for **1a** and dry toluene for **2a**) under reflux with stirring for 24 hr. After evaporation of the volatile materials in vacuo, the residual substance was collected and recrystallized from ethyl alcohol to give:

a) Yellow needles m.p. 105°C, yield 98% proved to be unchanged **1a**¹⁰ (m.p., mixed m.p. and comparative IR spectra).

b) Yellow needles m.p. 142°C, yield 97% proved to be unchanged **2a**¹¹ (m.p., mixed m.p. and comparative IR spectra).

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