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Hydrazinophosphorus Compounds IV. Reaction of Phosphoro- and Phosphino-hydrazides with Benzil and Benzil Monohydrazone

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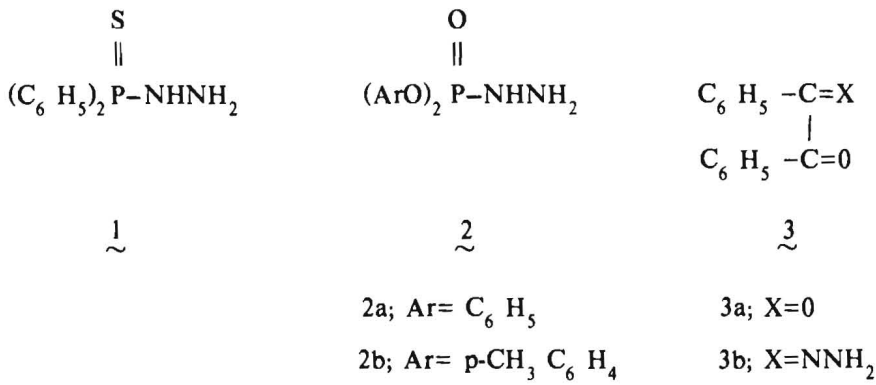
Hydrazinophosphorus compounds 1, 2 react with benzil 3a and benzil monohydrazone 3b, to yield mono- and bis-hydrazones 4, 5. In this respect, hydrazinophosphorus compounds behaved similar to arylhydrazines and in contrast to p'toluenesulfonylhydrazide. The latter hydrazide is known to react with benzil to yield only the bis-hydrazone. The structures of the new hydrazones 4, 5 have been confirmed by correct analytical data and IR spectral studies.

In connection with a general study of the chemistry of hydrazino-phosphorus compounds (El-Deek 1979), it was interesting to study the reaction of diphenylthiophosphino-hydrazide 1 and diarylphosphoro-hydrazides 2 with benzil 3a and benzil monohydrazone 3b.



1 2 3

2a; Ar= C_6H_5 3a; X=0

2b; Ar= p-CH_3 C_6H_4 3b; X=NNH_2

This investigation is of interest in particular, to compare the reactivity of hydrazinophosphorus compounds with sulfonly and arylhydrazines towards benzil and benzil monohydrazone.

While benzil monoarylhydrazones are known (El-Khadem *et al.* 1968) and prepared from benzil and the calculated amount of the arylhydrazine, benzil mono-p-toluenesulfonyl-hydrazone could not be prepared, even from benzil monohydrazone 3b and p-toluenesulfonly chloride. Also, benzil monoxime and monohydrazone did not react with p-toluenesulfonylhydrazide (Bartlett and Stevens, 1967).

Experimental

Melting points are uncorrected. Infrared spectra were recorded on Unicum SP 200 G Unit as KBr pellets. Phosphoro- and phosphino-hydrazides were prepared by condensation of the corresponding chloridate $(ArO)_2\overset{S}{\underset{\|}{P}}-Cl$ and $(C_6H_5)_2\overset{O}{\underset{\|}{P}}-CL$, respectively with hydrazine hydrate as previously described (Audrith *et al.*, 1955).

General Method of Preparation of Hydrazones 4, 5

In the preparation of the hydrazones 4, benzil or benzil monohydrazone 3 (0.01 mol) was boiled under reflux with the appropriate hydrazinophosphorus compound (0.01) mol) in ethanol (50 ml) for 3 hr. The hydrazones 4a generally separated from the cool concentrated solution and were collected and recrystallized from ethanol.Yield *Ca.* 80%.

Similarly, the bis-hydrazones 5 were prepared by refluxing benzil and two equivalents of the hydrazinophosphorus compound in 1-propanol for 5 hr. Yield 75-85 %.

Results and Discussion

The behavior of p-toluenesulfonyl-hydrazide was similar to arylhydrazines, the hydrazino-phosphorus compounds 1, 2 react with an equal amount of benzil 3a and benzil monohydrazone 3b to yield the corresponding hydrazones 4.

$C_6H_5-C=X$
$C_6H_5-C=NNHY$

4

4	X	Y
a	O	$(C_6H_5)_2P=S$
b	NNH_2	$(C_6H_5)_2P=S$
c	O	$(C_6H_5O_2)P=O$
d	NNH_2	$(C_6H_5O_2)P=O$
e	O	$(p\text{-}CH_3C_6H_4O_2)P=O$
f	NNH_2	$(p\text{-}CH_3C_6H_4O_2)P=O$

The reaction proceeds smoothly in refluxing ethanol in high yield (Ca 80%).

While benzil bis-arylhydrazones were obtained from benzil and excess arylhydrazine in acetic acid, benzil bis-thiophosphino- and bis-phosphoro-

hydrazones 5 were obtained by refluxing benzil in l-propanol and two equivalents of the necessary hydrazinophosphorus compound.

$C_6H_5-C=N-NH-A$

$CH-C=N-NH-A$

5

5	A
a	$(C_6H_5)_2P=S$
b	$(C_6H_5O)_2P=O$
c	$(p\text{-}CH_3C_6H_4O)_2P=O$

All the hydrazones are new crystalline compounds. Correct analytical data were in support of structures 4, 5. Besides, the ir measurements of the phosphorohydrazones 4c-f and 5b,c displayed strong band around 1200 cm^{-1} due to the P=O stretching vibration (a- Thomas, 1974). The P=S absorption for the thiophosphinyl hydrazones 4a,b and 5a appeared at 700 cm^{-1} (b- Thomas, 1974). All phosphorohydrazones showed strong P-O-Ar absorption at 980 cm^{-1} (c-Thomas 1974) whereas the P $-C_6H_5$ stretching absorption was observed for all thiophosphino derivatives at 1100 – 1130 cm^{-1} (Colthup *et al.* 1964). The monohydrazones 4a, c, e showed stretching frequencies at 1670 cm^{-1} and at 1620 cm^{-1} due to the C=O and C=N groups respectively. The IR spectra of all bis-hydrazones are devoid from the C =O absorption and showed the C=N stretching around 1620 cm^{-1}.

Table 1. Mono and bis-phosphorohydrazones of benzil and benzil monohydrazones 4 and 5.

Com-pound	M.p. (°C)	Molecular Formula	Analysis %N Calcd	%N Found	%P Calcd	%P Found
4a	120	$C_{26}H_{21}N_2OPS$	6.4	6.6	7.1	7.3
b	151	$C_{26}H_{23}N_4PS$	12.3	12.6	6.8	6.6
c	172	$C_{26}H_{21}N_2O_4P$	6.1	6.3	6.8	6.6
d	156	$C_{26}H_{23}N_4O_3P$	11.9	11.6	6.6	6.5
e	180	$C_{28}H_{25}N_2O_4P$	5.8	5.8	6.4	6.3
f	165	$C_{28}H_{27}N_4O_3P$	11.2	11.4	6.2	6.1
5a	226	$C_{38}H_{32}N_4P_2S_2$	8.4	8.2	9.3	9.5
b	164	$C_{38}H_{32}N_4O_6P$	8.0	8.1	8.8	9.0
c	170	$C_{42}H_{40}N_4O_6P$	7.4	7.2	8.2	8.0

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مركبات هيدرازينو الفوسفور-٤ - تفاعل الفوسفور والفوسفينو هيدرازيد مع البنزيل والبنزيل أحادي الهيدرازون

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المركبان ١ ، ٢ (هيدرازينو الفوسفور) يتفاعلان مع البنزيل والبنزيل أحادي الهيدرازون (٣) ليعطيا أحادي وثنائي الهيدرازون ٤ ، ٥ . مركبات هيدرازينو الفوسفور تتفاعل مثل أريلات الهيدرازون بعكس الباراسلفونيل هيدرازيد . الهيدرازيد الأخير معروف أنه يعطي ثنائي الهيدرازون مع البنزيل ثم تأييد تركيبات مركبات الهيدرازون الجديدة (٤ ، ٥) بالتحاليل الدقيقة وطيف الأشعة تحت الحمراء .