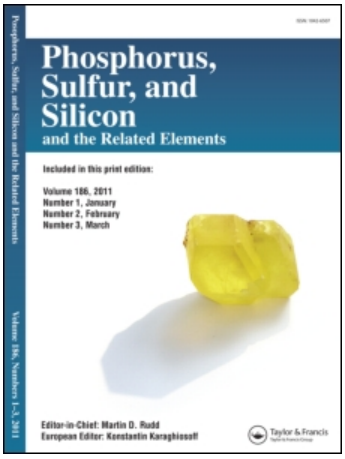

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A CONVENIENT AND NOVEL ONE-POT SYNTHESIS OF 3-OXO-P-1,5,3-DIAZAPHOSPHEPINES AND 3-THIOXO-P-1,5,3-DIAZAPHOSPHEPINES

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In a convenient one-pot sequence, treatment of benzil-dibenzylimine with sodium in dry tetrahydrofuran followed by addition of phosphorodichloridate and phosphorothiodichloridate yields 3-oxo-P-1,5,3-diazaphosphepines and 3-thioxo-P-1,5,3-diazaphosphepines, respectively.

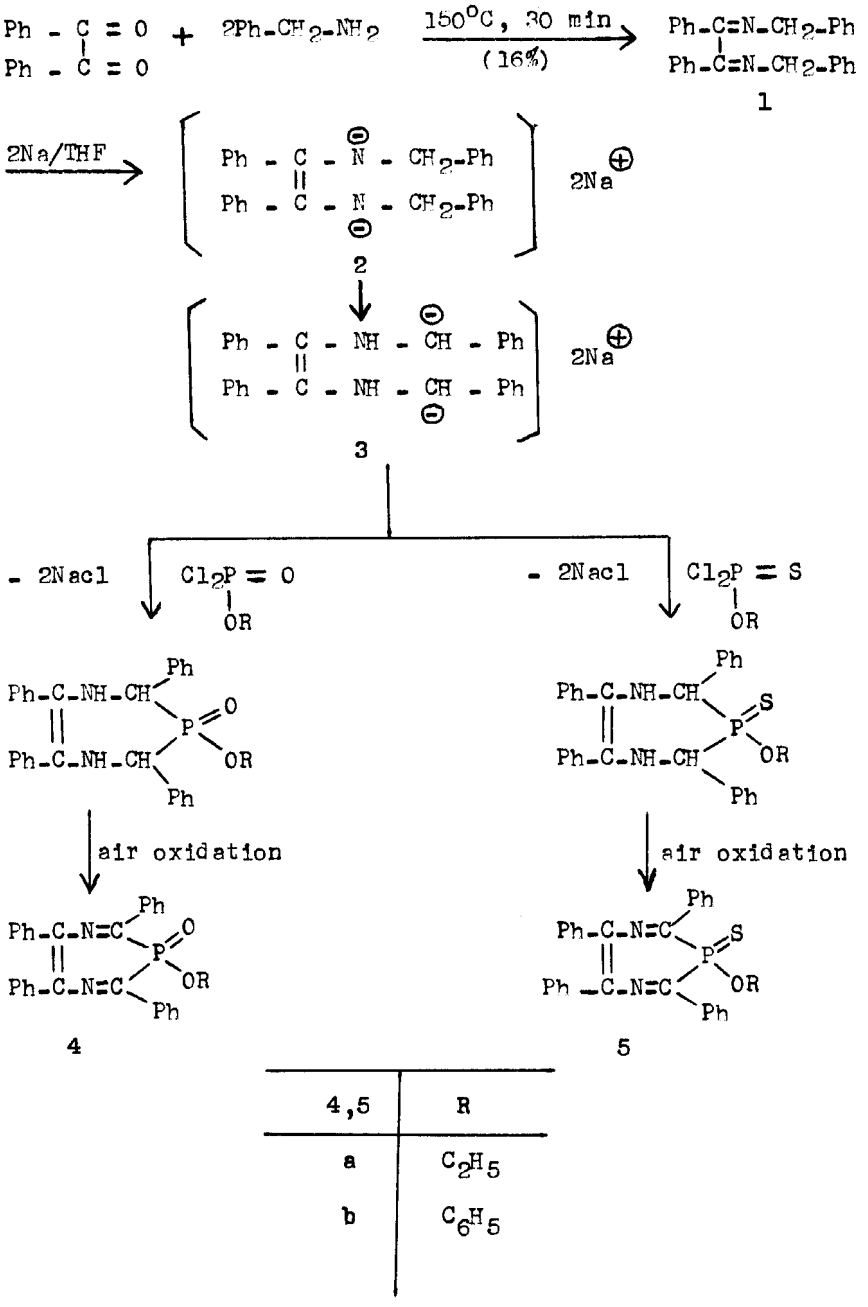
Key words: Benzil dibenzylimine; phosphorodichloridate; phosphorothiodichloridate; diazaphosphepines; spectral studies.

Seven membered ring system having two phosphorus atoms, 5H-dibenz [d,f]-[1,3]-diphosphepine has been synthesised by Mann and coworkers.[1,2] Dioxaphosphepines[3,4] have been screened for their biological activity. In continuation of previous studies on dioxaphospholes[5,6] and rarity of seven membered phosphorus heterocycles prompted us to synthesise the title compounds from the easily available benzil dibenzylimine which are not reported in the literature.

RESULTS AND DISCUSSION

The reaction of benzil dibenzylimine (1) with sodium in dry tetrahydrofuran followed by addition of ethyl phosphorodichloridate and phenyl phosphorodichloridate gives a solid material identified as 3-ethoxy-2,4,6,7-tetraphenyl-3-oxo-p-1,5,3-diazaphosphepine 4a and 3-phenoxy-2,4,6,7-tetraphenyl-3-oxo-p-1,5,3-diazaphosphepine 4b, respectively. The reaction of 1 with sodium in dry tetrahydrofuran followed by addition of ethyl phosphorothiodichloridate and phenyl phosphorothiodichloridate gives 3-ethoxy-2,4,6,7-tetraphenyl-3-thioxo-p-1,5,3-diazaphosphepine 5a and 3-phenoxy-2,4,6,7-tetraphenyl-3-thioxo-P-1,5,3-diazaphosphepine 5b, respectively.

This synthesis involves the initial formation of disodium salt 2 by the electron transfer from sodium to benzil-dibenzylimine 1 followed by intramolecular hydrogen abstraction gives the dianion[7] 3, which attacks phenyl or ethyl phosphorodichloridate and phenyl or ethyl phosphorothiodichloridate. Intramolecular nucleophilic attack with elimination of chloride ions (detected by the formation of silver chloride on addition of aqueous silver nitrate) leads to the formation of products 4 and 5. Compounds 4 and 5 were characterised on the basis of their satisfactory elemental analyses and spectral data (Table I).



4,5	R
a	C_2H_5
b	C_6H_5

TABLE I

Compounds 4 and 5 prepared

Product	Yield[a] (%)	mp (°C)	ir P=O	(Nujol) P = S	(cm^{-1}) (P-O-C)	^{1}nmr(CDCl$_3$/TMS)(PPm)
4a	56	232	1285	-	1030 1160	1.35(t,3H,J=7.1 Hz); 4.40(q,2H,J=7.1 Hz); 7.25(m,20H,arom.).
4b	58	239	1280	-	1220	7.45(m,25H,arom.).
5a	52	242	-	785	1040 1170	1.32(t,3H,J=7.1 Hz); 4.25(q,2H,J=7.1 Hz); 7.52(m,20H,arom.).
5b	54	246	-	790	1215	7.32(m,25H,arom.).

[a] Yields of isolated pure product.

TABLE II

Microanalytical data for compounds 4 and 5

Compound	Molecular formula	C Calc.(Found)	H Calc.(Found)	N Calc.(Found)
4a	$C_{30}H_{25}N_2O_2P$	75.55 (75.37)	5.24 (5.02)	5.87 (5.95)
4b	$C_{34}H_{25}N_2O_2P$	77.78 (77.63)	4.76 (4.56)	5.33 (5.20)
5a	$C_{30}H_{25}N_2OPS$	73.09 (72.92)	5.07 (4.85)	5.68 (5.80)
5b	$C_{34}H_{25}N_2OPS$	75.48 (75.28)	4.62 (4.44)	5.18 (5.07)

EXPERIMENTAL

All melting points were uncorrected. The ir and nmr spectra were recorded on a Perkin-Elmer 720 and JEOL JNM FX-90Q spectrophotometers, respectively. The microanalyses were carried out using Coleman carbon-hydrogen analyser and Coleman nitrogen analyser and were in satisfactory agreement with the calculated values which are given in Table II.

Benzil dibenzylimine (1), Procedure.[8] A mixture of benzil (4.2 g) and benzylimine (8 ml) was heated under nitrogen atmosphere for 30 min. at 150°C. After cooling, the mixture was heated with water to remove benzylamine and the material was taken in hot alcohol. Fractional crystallization from methanol gave three products: 2,3,5,6-tetraphenylpyrazine, mp 246°C; 1-benzyl-2,4,5-triphenylimidazole, mp 162–63°C and benzildibenzylimine (1), (0.70 g, 16%), mp 97°C.

$C_{28}H_{24}N_2$ Calc. C, 86.56; H, 6.29; N, 7.21
(388.5) Found C, 86.32; H, 6.07; N, 6.92%

IR (Nujol) ν (cm^{-1}): 1620 (C=N)
UV (Ethanol): λ max = 250 nm
^{1}HNMR ($CDCl_3$/TMS) δ (PPm): 4.60 (S, 4H, $2CH_2$); 7.65 (m, 20H, arom).

3-Ethoxy-and 3-phenoxy-2,4,6,7-tetraphenyl-3-oxo-P-1,5,3-diazaphosphepines 4a *and* 4b, *General Procedure.* Sodium pieces (1 g, 0.044 mole) are slowly added to dry THF (70 ml) in a three-necked round bottomed flask, fitted with a reflux condenser, a mercury trap and a pressure equalizing addition funnel with constant stirring under a nitrogen atmosphere. A solution of benzildibenzylimine 1 (2.3 g, 0.006 mole) in dry THF (10 ml) was added dropwise. Stirring at reflux temperature was continued for 5 h and the contents were allowed to cool. Ethylphosphorodichloridate (2 ml) and phenylphosphorodichloridate (2 ml) was slowly added and the mixture was heated under reflux for 1 h. The contents were allowed to stand at room temperature for about 2 h. THF was removed by distillation under reduced pressure, the residual matter was treated with ether. The ethereal layer was washed 2–3 times with water and dried with anhydrous sodium sulphate. The ether was removed on a rotary evaporator and the residual material was crystallised from benzene/petroleum ether (bP 40–60°C). Addition of silver nitrate to the aqueous layer gave a white precipitate of silver chloride.

3-Ethoxy- and 3-phenoxy-2,4,6,7-tetraphenyl-3-thioxo-P-1,5,3-diazaphosphepines 5a *and* 5b, *General Procedure.* In place of ethyl or phenyl phosphorodichloridate in the above method ethyl or phenyl phosphorothiodichloridate (2 ml) was slowly added and the products were crystallised from benzene/ethanol.

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