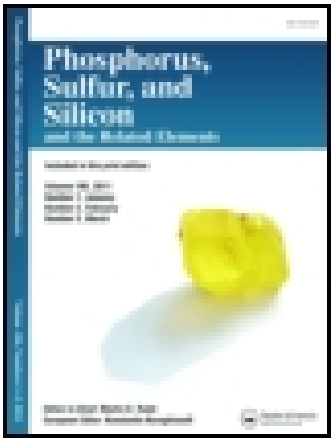

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REACTIONS OF CYCLODIPHOSPH(V)AZANES WITH PHENOLIC ALDEHYDES AND HYDROXYCINNAMONITRILE DERIVATIVES

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REACTIONS OF CYCLODIPHOSPH(V)AZANES WITH PHENOLIC ALDEHYDES AND HYDROXYCINNAMONITRILE DERIVATIVES

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Cyclodiphosphazane derivatives incorporated formyl and acrylonitrile moieties $2_{a,b}$, *4*, *5* are reported. Various (formylphenyl) N-arylphosphoramidic chloride esters 7_{a-e} were also prepared. The postulated mechanisms for the formation of such compounds are rationalized. Its U.V., IR ^{1}H-NMR and mass spectra were discussed.

Keywords: Hexachlorocyclodiphosphazanes; 2,4-dioxo-2-chloro-4-(formylphenoxy)-1, 3-diarylcyclodiphosphazanes; (formylphenyl) N-aryl-phosphoramidic chloride ester

Reactions of various nucleophilic reagents with hexachlorocyclodiphosph (v)azanes have attracted a great deal of interest[1–9]. In the present paper we utilize phenolic aldehydes and hydroxycinnamonitrile derivatives as nucleophiles to synthesize some new cyclodiphosphazane derivatives in which a formyl and acrylonitrile is incorporated as side chain.

Treatment of 1,3 di(p-anisyl) or (p -chlorophenyl)-2,2,2,4,4,4-hexachlorocyclodiphosph(v)azane (*1d,f*)[10,11] with p-hydroxy-benzaldehyde in acetonitrile without base or in dry benzene containing finally powdered sodium metal gave the corresponding 2,4-dioxo-2-chloro-4-(p-formylphenoxy)-1,3-diarylcyclodiphosphazane (*2a,b*) (Scheme 1). Condensation of 1f with p-hydroxycinnamonitrile in acetonitrile gave two products *3a* and *4*. The insoluble product was assigned structure *3a* while the second product *4* was obtained from the mother liquor after dilution with ether. This compound *4* gave analytical figures compatible with

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2,4-dioxo-2-chloro-4-[(p-methylidenemalononitrile)phenoxy]-1,3-di(p-chloro-phenyl)cyclodiphosphazane. The suggested structure *4* was confirmed by its independent synthesis from condensation of *2a* with malononitrile (m.p and m.m.p.). Also, the reaction of *1e* with p-hydroxybenzylidenemalononitrile in acetonitrile gave *3b* (Scheme 1).

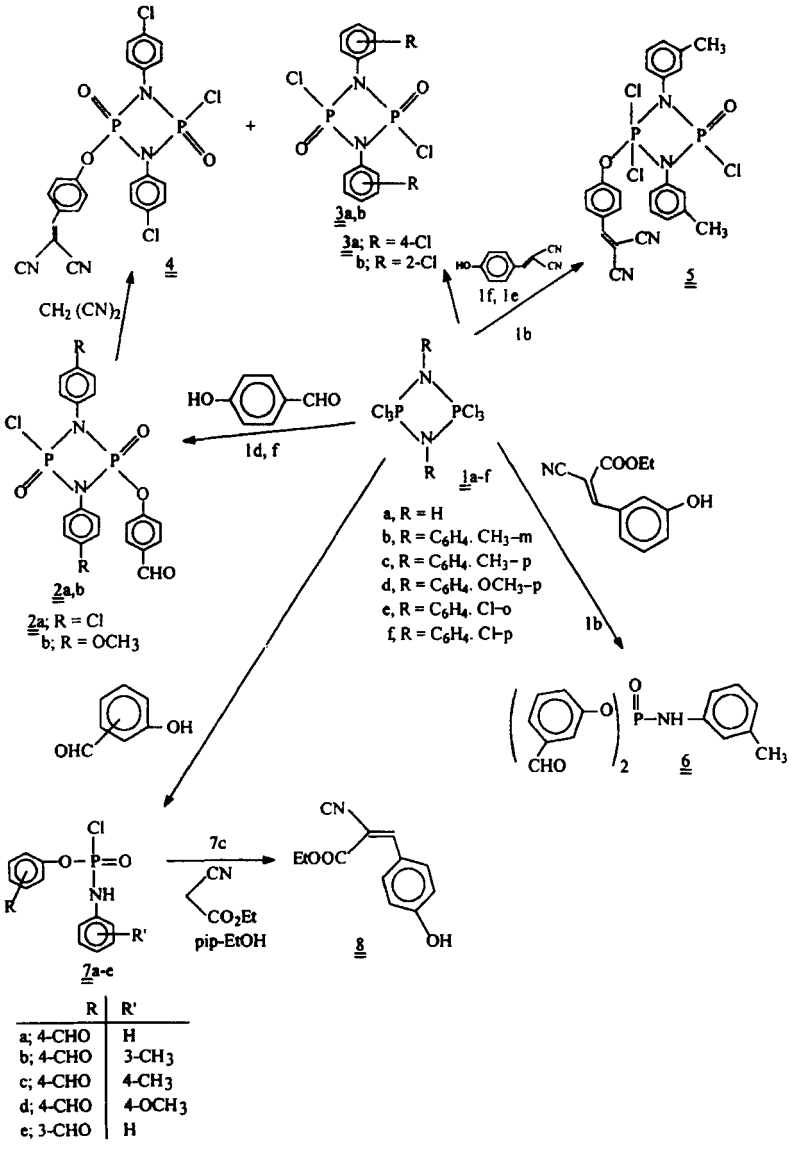
Interaction of *1b* with p-hydroxycinnamonitrile under the above reaction conditions afforded a product which was formulated as 1,3-di (m-tolyl)-2,4,4-trichloro-4-[(p-methylenemalononitrile)phenoxy]cyclo diphosphazane (*5*). While reaction of *1b* with m-hydroxybenzylidene ethyl cyanoacetate in acetonitrile gave one isolatable product O,O'-di (m-formylphenyl)-N-(m-tolyl)phosphoromonoamidate (*6*).

Condensation of *1* with phenolic aldehydes in boiling dry (benzene pyridine) or in acetonitrile afforded (formylphenyl) N-arylphosphoramidic chlonide ester of type *7*a-e (Scheme 1).

Finally, Condensation of (p-formylphenyl) N-p-tolylphosphoramidic chloride ester (*7c*) with ethyl cyanoacetate in absolute ethanol containing few drops of piperidine gave a product free phosphorus p-hydroxybenzylidene ethyl cyanoacetate (*8*) (Scheme 1).

TABLE I Spectral Data of Some New Compounds

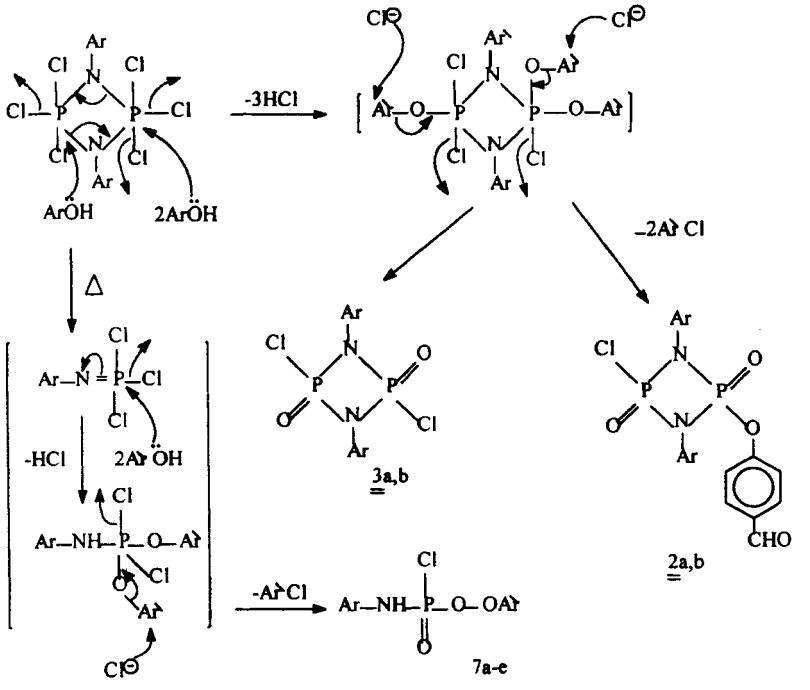
Compd	*Spectral Data*
2b	U.V. λ max (EtOH) (Log ∈) 239.5 (4.75), 287 [4.78) nm, IR γ_{max} at 1610 (CO), 1270 & 1245 (O=P-O), 1175 (P-O-C), 505 & 520 cm^{-1}.
4	U.V. λ max (EtOH) (Log ∈) 208 (4.67), 243 (4.6) & 296 (3.89) nm.
5	U.V. λ max (EtOH) (Log ∈) 202 (4.58), 225 (4.28) and 310 (4.48) nm. IR γ_{max} at 2230 (CN), 1590(C=O), 1215 (OPN2), 1170 and 980–950 (P-O-C arom), 522 (P-Cl) cm^{-1}.
6	U.V. λ max (EtOH) (Log ∈) 208 (4.43), 286 (4.41).
7a	^{1}H-NMR: δ at 6.92–8.26 (8H, m, Ar-H); 9.03 (1H, hump, O=P- NH); 9.82 (1H, s, CHO) ppm
7b	IR: γ_{max} at 3080 (NH); 1605 (C=O); 1250–1215 (O=P-O); 1170 and 920 (P-O-C, arom.); 510 cm^{-1} (P-Cl).
7c	IR: γ_{max} at 1605 (CO); 1215 (O=P-O); 1170 & 920 (P-O-C, arom.); 520 cm^{-1} (P-Cl), ^{1}H-NMR δ at 2.43 (3H, s, Ar-CH_3); 7.52, 7.37, 7.81 (8H, AB system, 2d, J_1 = 10.9, J_2 = 9 Hz Ar -H), 9.00 (1H, hump, NH); 9.93 (1H, s, CHO) ppm; MS : m/e: 309 ($M^{\oplus}$) (10%), 210 (100%), 196, 182, 176, 91, 76 & 65.
7d	U.V λ_{max} (Log ∈) 225 (3.64); 260 (3.86); 263 (3.9) nm, ^{1}H- NMR δ at 3.8 (3H, s, Ar-O-CH_3); 8.5 (1H, s, O=P-NH); 7.9–9.6 [8H, m, Ar-H; with two doublets at 7.17 & 7.82 (J = 8Hz]; 9.9 (1H, s, CHO) ppm.
7e	^{1}H-NMR δ at 7.38 (9H, m, Ar-H); 7.5 (1H, s, NH, exchangeable with D_2O); 7.90 (1H, s, CHO) ppm., MS: m/e: 295 $(M)^{\oplus}$ (O); 196 (100); 167, 77, 64 and 51.
8	^{1}H-NMR δ at 1.5 (3H, t, CH_3), 4.55 (2H, q, CH_2; J=6Hz), 6.90- 7.34, 8.06, 8.2 (4H, 3 sets of multiplets, Ar-H), 7.43 (1H, s, CH =) and 8.35 (1H, s, OH).



R	R'
a; 4-CHO	H
b; 4-CHO	3-CH_3
c; 4-CHO	4-CH_3
d; 4-CHO	4-OCH_3
e; 3-CHO	H

SCHEME 1

The mechanistic propability for the formation of products 2a,b, 3a,b and 7a-e assumed to follow as shown in (Scheme 2):



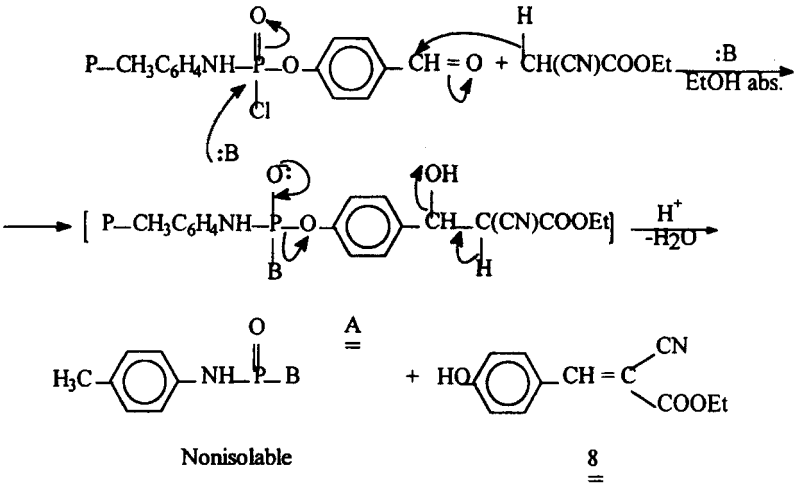
SCHEME 2

The formation of *8* took place as shown in (Scheme 3) through nucleophilic addition – elimination via the intermediate A under basic conditions

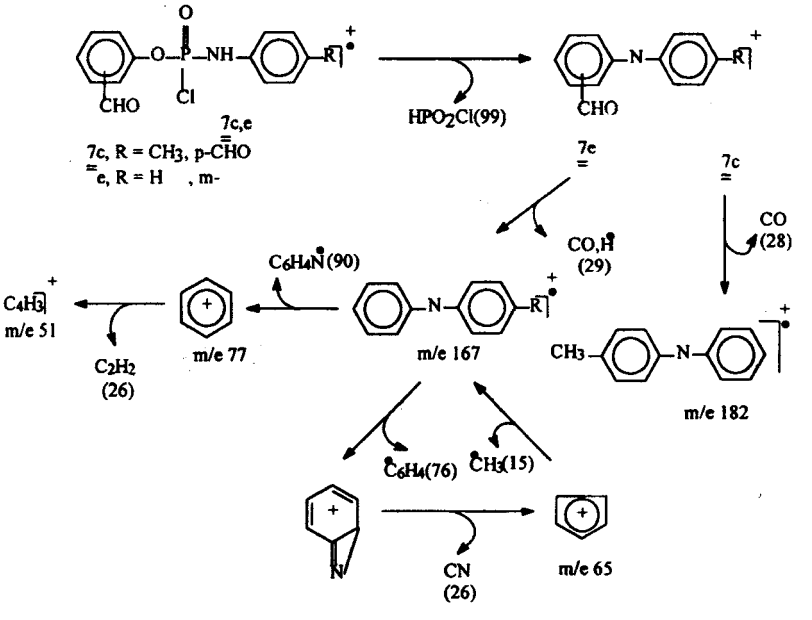
The mass spectral fragmentation of 7c,e is as shown. in (Scheme 4):

EXPERIMENTAL

The melting points are uncorrected, the U.V. spectra were measured in EtOH on Perkin Elmer Lambda 2UV/VIS spectrophotometer, IR spectra were measured (KBr disc) on a Pye-Unicam SP-1200 spectrophotometer



SCHEME 3



SCHEME 4

and ^{1}H-NMR spectra were measured on a varian EM-60MHz spectrometer at Al-Azhar University. Mass spectra were recorded on a varion MAT 711 spectrometer 70ev, direct inlet at Bayreuth University, Deutschland. Analytical data were determined in the microanalytical unit, Cairo University and are collected in Table II.

Hexachlorocyclodiphosphazanes $1_{a\text{-}e}$ were prepared by the method described by Chapman[10] and Kirsanov[11].

Condensation of Cyclodiphosphazanes *1* with phenolic aldehydes, p-hydroxybenzylidenemalononitrile and m-hydroxybenzylidene ethyl cyanoacetate (Table II).

Method A

To a mixture of *1* (0.005 mol) in dry benzene containing dry pyridine (2.4 ml), was added a solution of the phenolic aldehyde (0.045 mol) in dry benzene dropwise at room temperature with continuous stirring. The reaction mixture was refluxed for 6 hours then left overnight at room temperature. The formed pyridine, HCl was filtered off and the filterate was evaporated under reduced pressure. The residue was washed with ethanol and the obtained product was recrystallized from the proper solvent.

In case of 1_f, fine powdered sodium metal 58 mg (0.25 mol) in dry benzene (50 ml) was used instead of dry pyridine.

Method B

To a well stirred cold solution of *1* (0.005 mol) in acetonitrile (50 ml) was added a solution of phenolic aldehyde/or hydroxybenzylidene (0.045 mol) in acetonitrile (50 ml) in small portions during 1 hour. The reaction mixture was heated under reflux for 3 hours until the evolution of HCl gas almost completely ceased, then the reaction mixture was left overnight at room temperature and filtered. The filterate was evaporated under reduced pressure and the residue was triturated with ethanol and washed several times with dry diethyl ether and dried under vacuum.

In case of 1_f with p-hydroxybenzylidenemalononitrile, the reaction mixture was decanted, the residue washed with benzene, ethanol and pet. ether (60–80°) to give *3*a. Concentration of the decanted part and dilution with diethyl ether gave *4*.

TABLE II Analytical and Physical Data of Compounds *2-8*

Comp. No	*Type of Method*	*M.P. °C*	*Yield %*	*Formula (M. Wt)*	*Analysis Required/Found*		
					C%	*H%*	*N%*
2a	Aa	200	17	$C_{19}H_{13}Cl_{13}N_2O_4P_2$ (501.5)	45.46 45.30	2.59 2.60	5.58 5.60
b	Ba	225 (dec)	20	$C_{21}H_{19}ClN_2O_6P_2$ (492.5)	51.17 51.00	3.86 3.90	5.69 5.50
3a	Bb	250	40	$C_{12}H_8Cl_4N_2O_2P_2$ (416)	34.62 34.60	1.92 1.90	6.73 6.60
b	Bb	200	35	$C_{12}H_8Cl_4N_2O_2P_2$ (416)	34.62 34.50	1.92 1.90	6.73 6.60
*4**	Bb	184	15	$C_{22}H_{13}Cl_3N_4O_3P_2$ (549.5)	48.04 48.00	2.37 2.40	10.19 10.20
5	Bb	148	10	$C_{24}H_{19}Cl_3N_4O_2P_2$ (563.5)	51.11 51.00	3.37 3.40	9.94 10.00
6	Bb	125	40	$C_{21}H_{18}NO_5P$ (395)	63.80 63.80	4.56 4.66	3.54 3.60
7a	Bb	90	35	$C_{13}H_{11}ClNO_3P$ (295.5)	52.79 52.80	3.72 3.70	4.74 4.60
b	Bb	138	15	$C_{14}H_{13}ClNO_3P$ (309.5)	54.28 54.20	4.20 4.20	4.52 4.40
c	Ab	244	15	$C_{14}H_{13}ClNO_3P$ (309.5)	54.28 54.10	4.20 4.00	4.52 4.40
d	Ab	196	15	$C_{14}H_{13}ClNO_4P$ (325.5)	51.61 51.60	3.99 4.00	4.30 4.20
e	Bb	215	30	$C_{13}H_{11}ClNO_3P$ (295.5)	52.79 52.70	3.72 3.60	4.74 4.60
*8***	Ba	168	20	$C_{12}H_{11}NO_3$ (217)	66.36 66.40	5.07 5.00	6.45 6.50

Solvent: a-ethanol. b-dil-ethanol.

* An authentic sample was prepared from condensation of 2a (0.005 mol) in absolute ethanol (50 ml) and malononitrile (0.005 mol) in the presence of few drops of piperidine under reflux for 30 minutes (m.p., m.m.p.).

**Condensation of 2a (0.005 mol) in absolute ethanol (50 ml) and ethyl cyanoacetate (0.005 mol) in presence of few drops of piperidine under reflux for 30 minutes gave p-hydroxybenzylidene ethyl cyanoacetate 8. An authentic sample was prepared as usual manner from p-hydroxybenzaldehyde and ethyl cyanoacetate (m.p., m.m.p.).

Note: Compounds 2a,b, 7a,b are orange, 3a,b, 5, 6 are white, 4 is cream, 7c is yellow, 7d is golden yellow, 7e is brown, 8 is colourless.

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