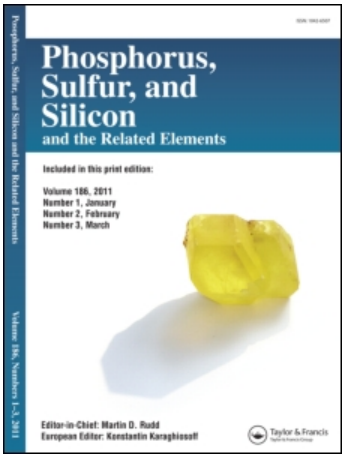

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NEW DERIVATIVES OF IMINOCYCLODIPHOSPHAZANE, CHLOROPHOSPHAZOBENZYLIDENECYANO-ETHYL KETONE AND DICINNAMOYLPHOSPHORTRIAMIDE

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NEW DERIVATIVES OF IMINOCYCLODIPHOSPHAZANE, CHLOROPHOSPHAZOBENZYLIDENECYANO-ETHYL KETONE AND DICINNAMOYLPHOSPHORTRIAMIDE

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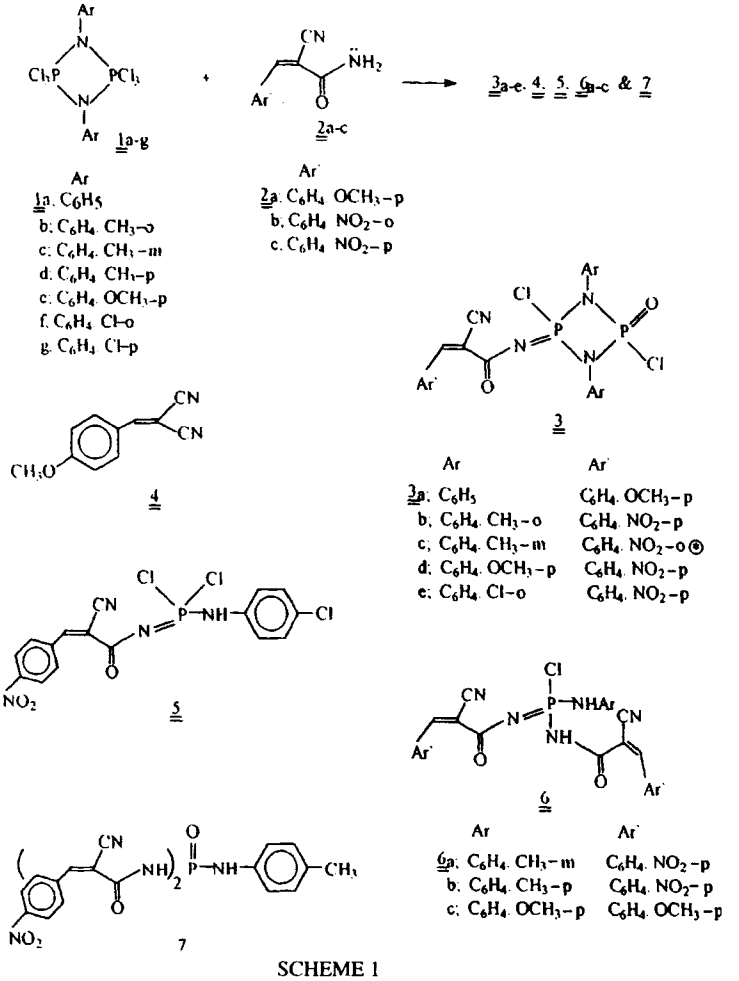
[(Arylidenecyanoacetyl)imino]cyclodiphosphazanes *3,4-chloroanilinodichlorophosphazo (4-nitrobenzylidene) cyanomethyl ketone 5, [(4-substituted benzylidenecyanoacetamido) (4-substituted anilino)] chlorophosphazobenzylidenecyanomethyl ketone 6 and di[(p-nitro-α-cyanocinnamoyl) (p-tolyl)]phosphortriamide 7 were synthesized from the reaction between cyclodiphosphazanes 1 and arylidene-cyano-acetamides 2. The postulated mechanism for the formation of such products were rationalized. The structures assigned were supported by UV, IR, ^{1}H NMR and mass spectra.*

Keywords: Hexachlorocyclodiphosphazanes; [(arylidenecyanoacetyl) mino]-cyclodiphosphazanes; phosphazobenzylidenecyanomethyl ketone; phosphortriamide; arylidenecyanoacetamides

Owing to the importance of organophosphorus derivatives in medical and pesticidal chemistry[1–3], considerable effort has been invested in their preparations. It was found that phosphorus pentachloride and phenyltetrachlorophosphorane reacted with arylidenecyanoacetamides to give trichlorophosphazo and phenyldichlorophosphazoarylidenecyano-acetamides respectively[4,5].

In the present search we synthesized some new iminocyclodiphosphazanes, phosphazocyanomethyl ketone and cinnamoylphosphortriamides with the expectation of biologically activity.

Hexachlorocyclodiphosph(V)azanes 1[6,7] employed as starting compounds underwent nucleophilic substitution with arylidenecyano-acetamides 2 (Scheme 1) to give 1,3-diaryl-2,4-dichloro-2-oxo-4-[(arylidenecyanoacetyl) imino]cyclodiphosphazanes 3 as the main product. The formation of such compounds indicates that the amide group is the most active center. The proposed mechanism (Scheme 2; route A) is supported by the isolation of p-anisylidenemalononitrile 4 from the reaction mixture between 1 and 2a as the only isolatable product.

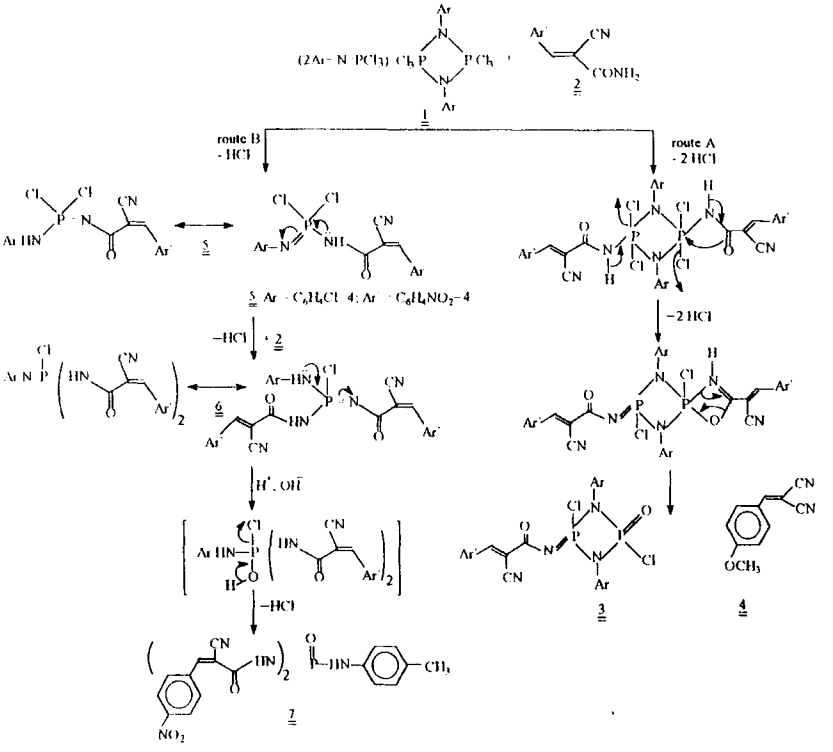


SCHEME 1

* Skins burns result from contact during characterization of 3c (extremely irritant)

The condensation of 1,3-di(4-chlorophenyl)hexachlorocyclodiphosphazane 1g with 4-nitrobenzylideneczyanoacetamide 2c in acetonitrile gave one isolatable product which was formulated as 4-chloroanilinodichlorophosphazo(4-nitrobenzylidene) cyanomethyl ketone 5 for which cyclodiphosphazane ring is scission, however interaction of 1,3-diarylcyclodiphosphazanes 1 with 4-substitutedarylidenecyanoacetamides 2c,a in acetonitrile gave the corresponding [(4-substituted benzylidenecyanoacetamido) (4-substituted anilino)]chlorophosphazobenzylidenecyanomethyl ketone 6 respectively. In the case of reaction between 1 and 2c a solid product which precipitated gave analytical figures compatible with di[(4-nitro-α-cyano)cinnamoyl (4-tolyl)] phosphortriamide 7.

The formation of such compounds 5-7 (Scheme 2; route B) was explained through the dissociation of the dimeric cyclodiphosphazane ring to monophosphazane under the reaction conditions, was followed by stepwise nucleophilic substitution at the phosphazenyl center in a similar fashion as at the phosphoryl or thiophosphoryl center which generally proceeds by an associative S_N2 (p) mechanism with a fivecoordinate intermediate[8]



SCHEME 2

The structure of the prepared compounds were confirmed from their analytical, UV, IR, ^{1}H NMR and mass spectrometric data. They are collected in table I and table II.

EXPERIMENTAL

The melting points were not corrected, the UV spectra were measured in EtOH on Perkin Elmer Lambda 2UV/VIS spectrophotometer, IR spectra were obtained (KBr disc) on a Pye-Unicam SP–1200 spectrophotometer and ^{1}H NMR spectra

were measured on a Varian EM–60MHz spectrometer at Al-Azhar University. Mass spectra were recorded on a Varian 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 were prepared by the method described by Chapman[6] and Kirsanov[7].

Cyclodiphosphazanes (3), chloro-, dichlorophosphazobenzylidene-cyanomethyl ketones (6), (5) and phosphortriamide derivative (7), (Table II).

To a well stirred cold solution of 1 (0.005 mol) in acetonitrile (50 ml) was added a solution of 2 (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 filtrate was evaporated under reduced pressure and the residue was triturated with ethanol and washed several times with dry diethyl ether and dried under vaccum.

TABLE I Spectral Data of Compounds 3-7

Compd	Spectral Data
3a	^{1}H NMR (DMSO-d_6): δ 3.88 (s, 3H; Ar-OCH_3); δ (7.05-8.10) (m, 14H; Ar-H), δ 8.17 (s, 1H, CH=C(CO)(CN))
3b	^{1}H NMR: δ 2.13 & 2.43 (2s, 6H, 2Ar-CH_3), δ (7.25-7.47), (8.45-8.87) (confused, 13H, Ar-H & CH=C(CO)(CN)). MS: m/z 573 (M^+) (0%), 460, 370, 355, 240, 153, 77, 65
3c	MS: m/z 574 (M^+) (0%), 503, 457, 442, 307, 199 (100%), 157.
3d	^{1}H NMR: δ 3.73 & 3.85 (2s, 6H, 2 CH_3O. Ar), δ (6.93-7.03) & (7.90-8.25) (two sets of multiplets, 12H, Ar-H), δ 8.35 (s, 1H, CH=C(CN)(CO))
3e	UV λ_{max} (EtOH) Log ε: 209 (4.44), 234 (4.19), 284 (4.2). MS: m/z 615 (M^+) (0%), 578, 550, 522, 487, 392, 309, 217, 216, 168

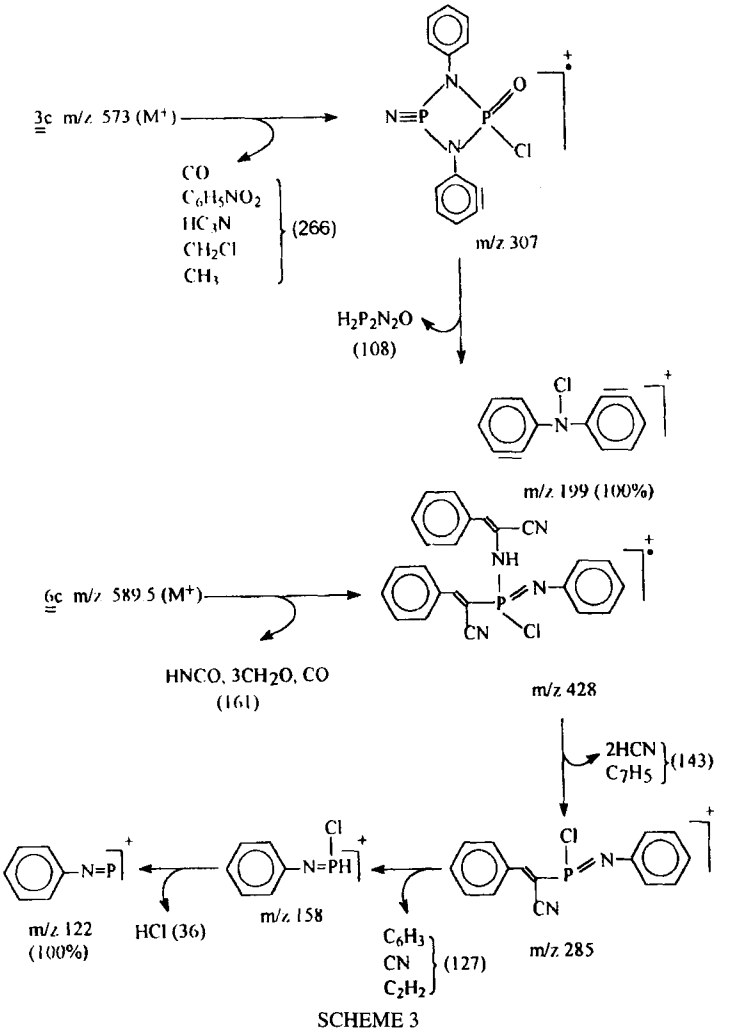
4	^{1}H NMR: δ 3.97 (s, 3H, Ar-OCH_3), δ 7.10, 7.27, 8.08, 8.20 (AB-pattern of two distorted doublets, 4H, Ar-H; J=10.2 Hz), δ 8.38 (s, 1H, CH=). MS: m/z 184 (M^+) (100%), 169 (M^+-CH_3), 141 (M^+-CH_3-CO), 115 (M^+-CH_3-CO-CN), 63 ($M^{\oplus}$-CH_3-CO-CN-CN-C_2H_5)
5	^{1}H NMR: δ (7.20-7.65) & (8.45-8.63) (2 sets of multiplets, 8H, Ar-H with two doublets at (7.60, 7.65) & (8.45, 8.50) J=3Hz), δ 8.33 (s, 1H, CH=C(CN)(CO)), δ 10.94 (hump, 1H, NHP(Cl)(Cl))
6a	^{1}H NMR: δ 2.27 (s, 3H, Ar-CH_3), δ (7.10-7.23) (hump, 2H, P(NH)(NH)), (7.10-8.83) (m, 12H, Ar-H; the p-nitrophenyl protons appeared in set of doubletsform at δ 8.40 & 8.45, J= 3Hz; δ 8.16 & 8.20; J= 2.4Hz; δ 8.55 & 8.60; J= 3Hz and at δ 8.80 & 8.83; J= 1.8Hz), δ (8.20-8.33) (confused, 2H, 2CH=C(CO)(CN)) MS: m/z 603.5 (M^+) (0%), 480, 430, 308, 170.
6b	IR: γNH & γCH aliph. & arom. [(2800-3300); broad], γCN [(2232), v.w. due to the presence of α CO group and conjugation with C=C & C=O], γC=C (1600), γNO_2 (two strong bands at 1525 & 1350), γP=N (1115) and γP-Cl (515). ^{1}HNMR: δ 2.37 (s, 3H, CH_3-Ar), (7.00-7.40) (m, 12H, Ar-H), δ 8.23 [(confused, 4H, 2CH=C(CN)(CO) & (-$NH)_2$N=], MS: m/z 603.5 (M^+) (0%), 308, 240 (100%).
6c	UV λ_{max} EtOH (Log ε): 232 (4.43), 344.5 (4.44). MS: m/z 589.5 (M^+) (0%), 428, 285, 158, 122 (100%)
7	^{1}H NMR: δ 2.40 (s, 3H, CH_3-Ar), δ (7.00-7.45), (8.33-8.40) & 9.27 (complex pattern with three sets, 12Ar-H, $(-NH)_3$ P=O, CH=C(CN)(CO))

TABLE II Analytical and Physical Data of Compounds (3–7)

Compd. No	*M.P. oC*	*Colour*	*Yield %*	*Formula (M. Wt)*	*Analysis Required/Found*			
					C%	*H%*	*N%*	*P%*
3a	168–170	yellow	65	$C_{23}H_{18}N_4P_2O_3Cl_2$	51.98	3.39	10.55	11.68
				(531)	52.00	3.40	10.60	11.70
3b	14() (dec.)	orange	7()	$C_{24}H_{19}N_5P_2O_4Cl_2$	50.17	3.31	12.20	10.80
				(574)	50.00	3.40	12.20	10.70
3c	105 (dec.)	yellow	63	$C_2H_{19}N_5P_2O_4Cl_2$	50.17	3.31	12.20	10.80
				(574)	50.10	3.40	12.10	10.80
3d	160	yellow	54	$C_{24}H_{19}N_5P_2O_6Cl_2$	47.52	3.14	11.55	10.23
				(606)	47.50	3.00	11,50	10.30
3e	90 (dec.)	orange	60	$C_{22}H_{13}N_5P_2O_4Cl_4$	42.93	2.11	11.38	10.08
				(615)	42.90	2.00	11.40	10.00
4*	116	yellow	25	$C1_{11}H_8N_2O$	71.74	4.35	15.22	
				(184)	71.80	4.40	15.00	
5	178 (dec.)	orange	25	$C_{16}H_{10}N_4P\ O_3Cl_3$	43.29	2.25	12.63	6.99
				(443.5)	43.20	2.20	12.60	7.00
6a	95	yellow	65	$C_{27}H_{19}N_7P\ O_6Cl$	53.69	3.15	16.24	5.14
				(603.5)	53.70	3.10	16.20	5.20
6b	140 (dec.)	yellow	30	$C_{27}H_{19}N_7P\ O_6Cl$	53.69	3.15	16.24	5.14
				(603.5)	53.80	3.00	16.30	5.10
6c	140 (dec.)	orange	55	$C_{29}H_{25}N_5P\ O_5Cl$	59.03	4.24	11.87	5.26
				(589.5)	59.00	4.10	11.90	5.30
7	192 (dcc.)	deep	25	$C_{27}H_{20}N_7P\ O_7$	55.38	3.42	16.75	5.30
		orange		(585)	55.40	3.40	16.80	5.20

* All the above reactions are unsuccessful in dry benzene as medium and in this case the reaction was carried in acetonitrile, where (4) is the only isolatable product. An authentic sample of (4) was obtained directly from p-anisaldehyde and malononitrile in ethanol/piperidine (m.p. & m.m.p).

Spectrometric fragmentation of 3c and 6c



SCHEME 3

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