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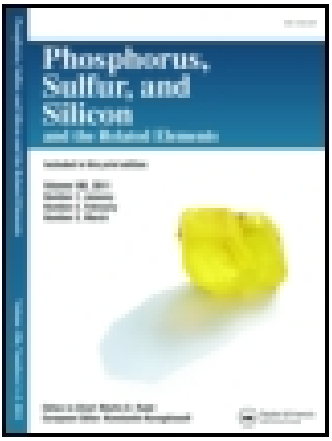

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SYNTHESIS AND INSECTICIDAL ACTIVITY OF NOVEL ACRYLONITRILE DERIVATIVES

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SYNTHESIS AND INSECTICIDAL ACTIVITY OF NOVEL ACRYLONITRILE DERIVATIVES

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(E)-3-*p*-Anisyl-2-cyano-2-propenoyl chloride and/or azide (1b and c) underwent successful nucleophilic displacement reactions, with urea and thiourea derivatives to give the mono- or di- displacement products (4, 8, 2 and 5) respectively, beside other cyclic products (3 and 6); with aromatic binucleophilies e.g. o-phenylene diamine, the expected di-displacement products (12 and 13) were obtained, while with 2-aminophenol a mixture of two mono-displacement products (15 and 16) were isolated.

Biological studies of diaryl ureas[1,2] urethanes[3,4] and heterocyclic systems like, pyrimidinones,[5,6] and benzimidazoles[7,8] as agrochemicals, pesticides and insecticides have been recently reported.

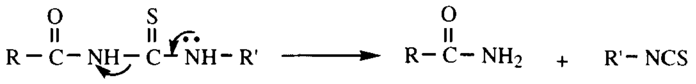
In continuation of our interest[9-11] on the synthesis and reactions of 2-propenoyl chloride and/or its azide derivatives, I report here the reactivity of (E)-3-*p*-anisyl-2-cyano-2-propenoyl chloride (**1b**) and its azide (**1c**) towards some organic reagents aiming to produce new acrylonitrile derivatives which might have enhanced biological activities.

(E)-3-*p*-Anisyl-2-cyano-2-propenoylazide (**1c**) reacted with urea via nucleophilic displacement of the azido group to give a mixture of N,N′-disubstituted urea (**2**) and its cyclization product 1,3,5-oxadiazin-4-one (**3**). Treatment of **2** with phosphoryl chloride afforded **3** in quantitative yield, (Scheme 1).

Reaction of **1c** with thiourea proceeded normally providing not only the di-displacement product (**5**) but also the mono-displacement product (**4**), besides the pyrimidinone derivative (**6**), which can be formed through cycloaddition of the free amino group onto the double bond in the α,β-unsaturated nitrile (**4**). Treatment of **5** with phosphoryl chloride or piperidine in ethanol, and also fusion of **4** at 180°C, afforded 1,3,5-oxadiazin-4-thione derivative (**7**) in good yield (Scheme 1).

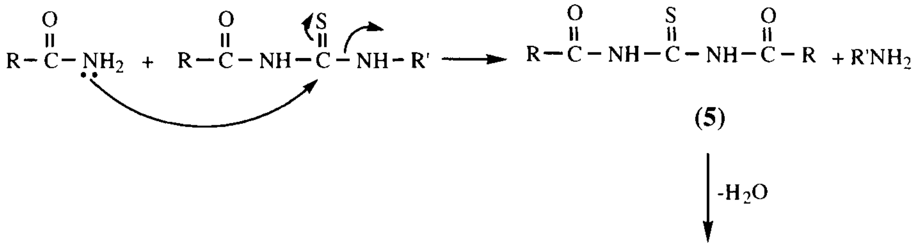
Reaction of **1c** with methylthiourea produced a mixture of the expected mono-displacement product (**8**) and the di-displacement product (**5**).

The formation of **5** and/or **7** from the mono-displacement products (**4**) and/or (**8**) can be interpreted by the following mechanism:

i) 

$$R-\overset{\overset{O}{\|}}{C}-NH-\overset{\overset{S}{\|}}{C}-NH-R' \longrightarrow R-\overset{\overset{O}{\|}}{C}-NH_2 + R'-NCS$$

4) $R' = H$
8) $R' = CH_3$

ii) 

$$R-\overset{\overset{O}{\|}}{C}-NH_2 + R-\overset{\overset{O}{\|}}{C}-NH-\overset{\overset{S}{\|}}{C}-NH-R' \longrightarrow R-\overset{\overset{O}{\|}}{C}-NH-\overset{\overset{S}{\|}}{C}-NH-\overset{\overset{O}{\|}}{C}-R + R'NH_2$$

(5)

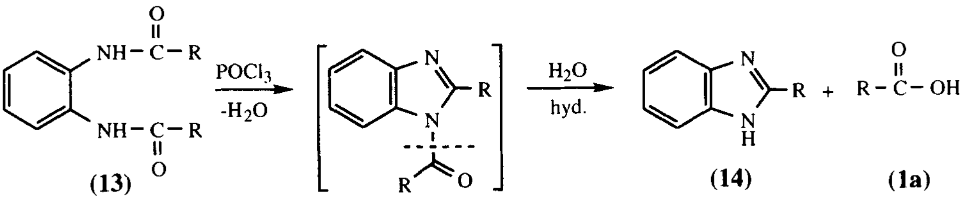
(7)

Furthermore, with allylthiourea, azide (**1c**) decomposes to give **9** (Scheme 1).

In the same manner **1c** reacted either with β-alanine or methylcarbamate producing the corresponding N-(2-propenoyl)-β-alanine derivative (**10**) and urethane derivative (**11**) respectively (Scheme 1).

o-Phenylene diamine reacted with **1c** to give a mixture of N,N-disubstituted derivative (**12**) and N,N'-disubstituted product (**13**) (Scheme 2).

Treatment of **13** with phosphoryl chloride afforded the 1H-benzimidazole derivative (**14**) via the following pathway:



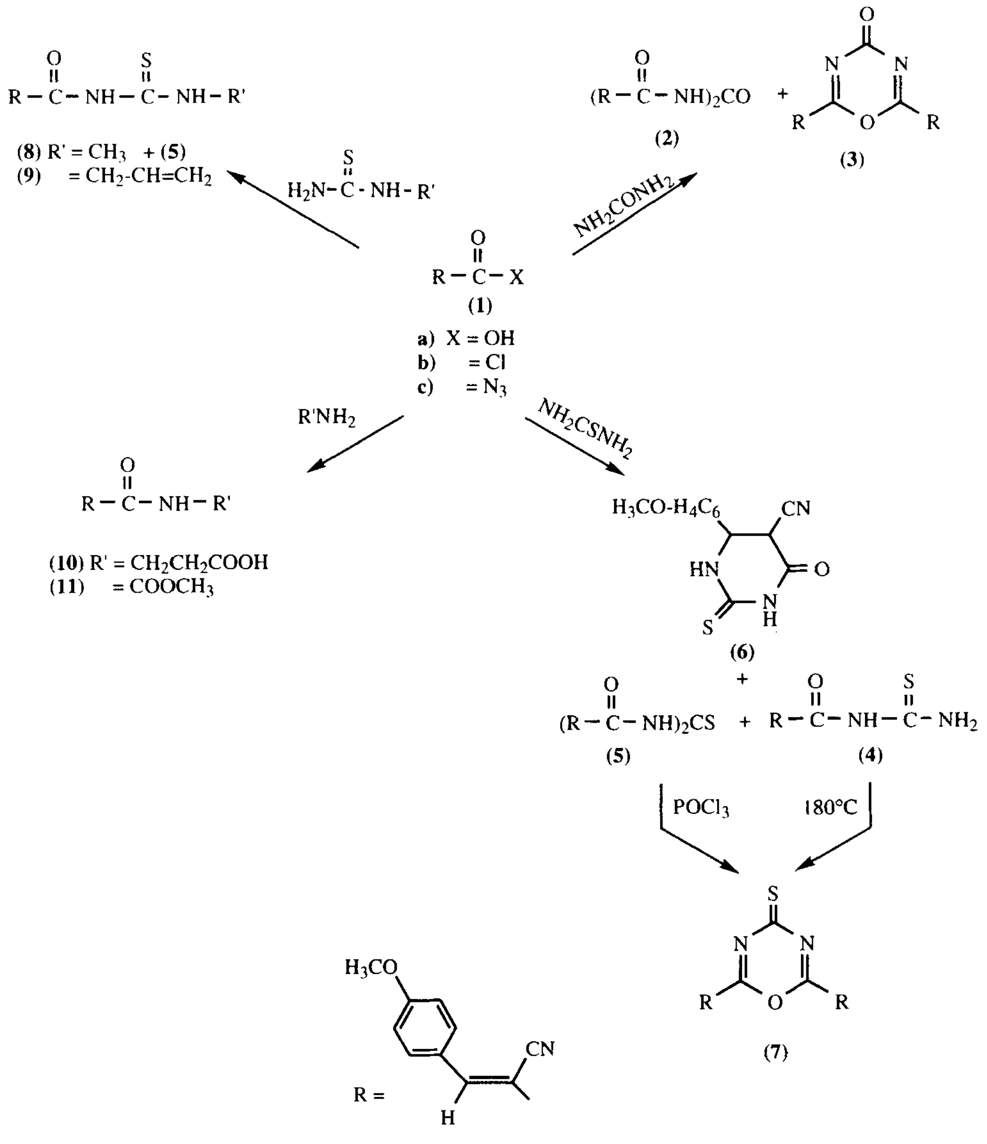
On the other hand, decomposition of azide (**1c**) with 2-aminophenol yielded a mixture of 2-aminophenyl propenoylate derivative (**15**) and N-(2-hydroxyphenyl)-2-propenoylamide derivative (**16**) (Scheme 2). Similarly, decomposition of **1c** with phenols, namely, phenol, 2-chlorophenol and *p*-cresol yielded the expected aryl 2-propenoylate derivatives (**17a–c**) respectively (Scheme 2).

In all of the previous reactions, the decomposition of the azide (**1c**) proceeds via an azide-displacement, the products being obtained from the reaction of the acid chloride (**1b**) with the same reagents. The favoring displacement in our case rather than azide decomposition via Curtius rearrangement may be due to the presence of the azide group cis- to the hydrogen atom, the fact means that there is no steric inhibition for nucleophilic substitution of the azide group.[11]

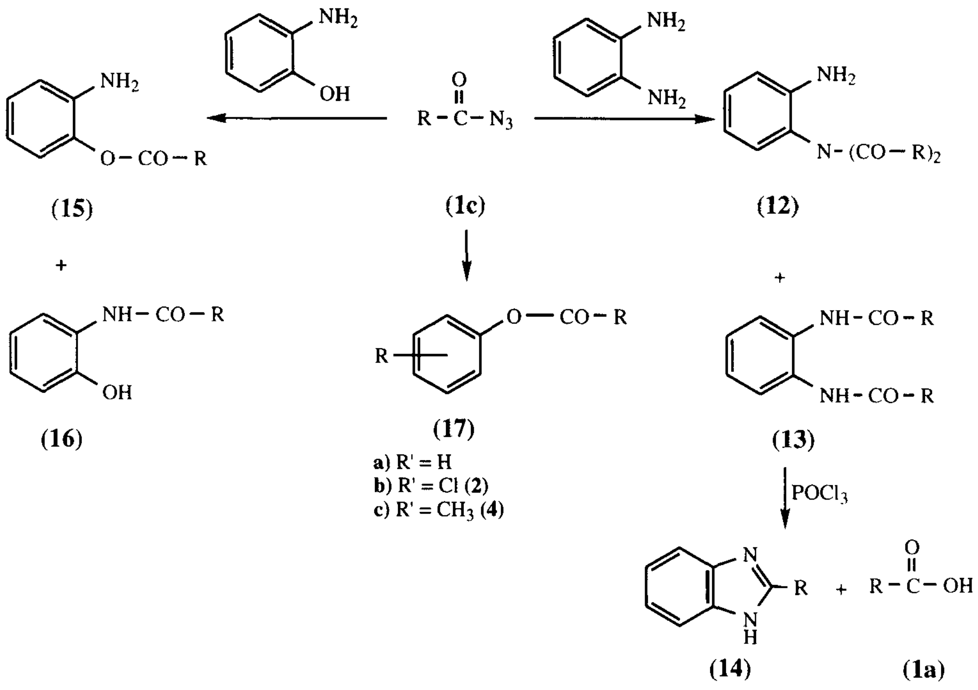
LARVICIDAL ACTIVITY

Materials and Methods

The biological activity of 10 organic compounds against *Culex pipiens* larvae was


(8) R' = CH3 + (5)
(9) = CH2-CH=CH2
H2N-C(=S)-NH-R'
(R-C(=O)-NH)2CO
(2)
(3)
NH2CONH2
(1)
a) X = OH
b) = Cl
c) = N3
R'NH2
NH2CSNH2
(10) R' = CH2CH2COOH
(11) = COOCH3
H3CO-H4C6
CN
(6)
(R-C(=O)-NH)2CS
(5)
R-C(=O)-NH-C(=S)-NH2
(4)
POCl3
180°C
(7)
H3CO
R =

Scheme 1



(Scheme 2)

determined using the WHO test technique. *Culex pipiens* larvae used in this study were collected from 6 October City, Giza Gov.. They were reared in insectary for one generation by standard technique. The larvae were fed on a mixture of dog biscuit, dried milk and yeast. Late third and early fourth instar larvae were kept in appropriate concentrations of a compound water mixture for a period of 24 hours. Six different concentrations of the selected organic compounds were used in the bioassay tests. In each test, 25 mosquito larvae put in glass jar with 250 ml tape water were treated with the compounds. Each test was replicated four times according to the standard testing procedure recommended by the WHO[12] (1975). The dead larvae were removed and mortality was calculated. Total percent mortality was corrected using Abbott's formula[13] (1925).

The results obtained in the table **4** show the relative toxicity of 10 compounds. The most effective compounds are no. **12** and **11**, followed by no. **7**, **17c** and **2**.

EXPERIMENTAL

All melting points are uncorrected. IR spectra were measured on Pye Unicam SP 200 G spectrometer with KBr Wafer technique. ^{1}H-NMR and ^{13}C-NMR spectra were determined on a Varian FT-200 spectrometer, with Dept experiment. All chemical shifts (δ) are expressed in ppm. All NH or OH protons disappeared by deuterium exchange (addition of D_2O). Mass spectra were determined on a Shimadzu, Single focusing mass spectrometer (70 ev).

N,N'-Bis(3-p-anisyl-2-cyano-2-propenoyl)urea (**2**) *and 2,6-bis[(2'-p-anisyl-1'-cyano)-ethen-1'-yl]-1,3,5-oxadiazin-4-one* (**3**)

A mixture of 3-*p*-anisyl-2-cyano-2-propenoyl azide[11,14] (**1c**) or the acid chloride[11,14] (**1b**) (0.01 mol) and urea (0.01 mol) in dry benzene (50 ml) was refluxed for 6 h. The solvent was removed and the residue was triturated with toluene to give **2** as colorless crystals (toluene) and **3** as yellow crystals (ethanol).

Conversion of **2** *into* **3**

A mixture of **2** (1 g) and phosphoryl chloride (10 ml) was heated on a water-bath for 8 h. After cooling the reaction mixture was poured into crushed ice (50 g). The solid separated was filtered, washed with water (2 × 20 ml), dried and crystallized from ethanol to give **3** in 98% yield.

N-(3-p-Anisyl-2-cyano-2-propenoyl)thiourea (**4**), *N, N'-bis(3-p-anisyl-2-cyano-2-proenoyl)thiourea* (**5**) *and 6-p-anisyl-5-cyano-2-thioxo-hexahydropyrimidin-4-one* (**6**)

A mixture of **1c** or **1b** (0.01 mol) and thiourea (0.01 mol) in dry benzene (50 ml) was refluxed for 30 min. The solid separated was filtered and crystallized from ethanol to give **4** as colourless crystals. The solid separated after concentration of the filtrate was collected and triturated with petroleum-ether 60–80°C-benzene mixture to give **5** as colorless crystals (toluene) and **6** as colorless crystals (petroleum-ether 60–80°C-benzene mixture). MS of **6**: m/z (262, 17%), M^+ (261, 94%), (245, 14%), M-NCS (203, 16%), M-NH_2CSNH_2 (186, 100%), (158, 43%).

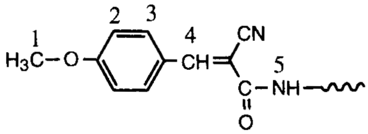
TABLE I

Physical data of compounds prepared

Compd. No.	m.p.°C (Yield%)	Molecular formula (M. wt.)	Analysis % Calcd/ Found			IR spectra V (cm^{-1})			
			C	H	N	NH,OH	C-N	C=O	C=S
2	202 dec.	$C_{23}H_{18}N_4O_5$	64.18	4.22	13.02	3490	2245	1710	-
	(48)	(430.42)	63.81	4.41	12.90	3350		1685	-
3	185-187	$C_{23}H_{16}N_4O_4$	66.99	3.91	13.59	-	2220	1796	-
	(16)	(412.40)	67.00	3.82	13.70				
4	178-180	$C_{12}H_{11}N_3O_2S$	55.16	4.24	16.08	3430	2240	1685	1180
	(60)	(261.31)	55.30	4.16	15.99	3200			
5	195 dec.	$C_{23}H_{18}N_4O_4S$	61.82	4.06	12.55	3400	2230	1680	1175
	(30)	(446.49)	61.89	3.90	12.47	(br)			
6	161-162	$C_{12}H_{11}N_3O_2S$	55.16	4.24	16.08	3375	2245	1700	1190
	(12)	(261.31)	54.92	4.33	16.21	(br)			
7	213-215	$C_{23}H_{16}N_4O_3S$	64.47	3.76	13.08	-	2200	-	1179
	(89)	(428.47)	64.51	3.92	12.95				
8	136-138	$C_{13}H_{13}N_3O_2S$	56.71	4.76	15.26	3400	2200	1680	1170
	(8)	(275.33)	56.82	4.81	15.01	3250			
9	133-135	$C_{15}H_{15}N_3O_2S$	61.01	5.12	14.23	3420	2220	1695	1185
	(36)	(295.22)	60.90	5.33	14.51	3275 [br]			
10	163 dec.	$C_{14}H_{14}N_2O_4$	61.31	5.13	10.21	3600-	2205	1735	-
	(66)	(274.28)	61.42	4.99	10.41	2500 (br)			
11	98-99	$C_{13}H_{12}N_2O_4$	60.00	4.65	10.76	3500	2220	1738	-
	(97)	(260.25)	59.79	4.50	10.62	(br)		1720	
12	199-201	$C_{28}H_{22}N_4O_4$	70.28	4.62	11.71	3300	2215	1685	-
	(15)	(478.51)	70.31	4.77	11.61	3420	2220		
13	229-230	$C_{28}H_{22}N_4O_4$	70.28	4.62	11.71	3320	2218	1690	-
	(63)	(478.51)	70.15	4.55	11.92		2224		
14	250-252	$C_{17}H_{13}N_3O$	74.17	4.76	15.26	3440	2222	-	-
	(75)	(275.31)	74.02	4.88	15.09				
15	182-183	$C_{17}H_{14}N_2O_3$	69.32	5.82	9.52	3400	2242	1700	-
	(75)	(294.31)	70.01	5.71	9.43	3250			
16	215-217	$C_{17}H_{14}N_2O_3$	69.32	5.82	9.52	3340	2200	1670	-
	(18)	(294.31)	69.51	5.99	9.61				
17a	123-124	$C_{17}H_{13}NO_3$	73.11	4.69	5.02	-	2200	1740	-
	(75)	(279.30)	72.89	4.80	5.30				
17b	152-154	$C_{17}H_{12}ClNO_3$	65.08	3.86	4.46	-	2222	1750	-
	(82)	(313.74)	64.82	3.99	4.43				
17c	134-136	$C_{18}H_{15}NO_3$	73.71	5.15	4.78	-	2200	1740	-
	(79)	(293.32)	73.61	5.39	4.59				

TABLE II

^{1}H-NMR data of prepared compounds

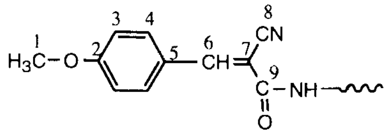


Compd. No.	CH_3(s)	C_2-H(d)	C_3-H(d)	C_4-H(s)	NH(s_{br})	Other protons
2	3.86	7.18	8.12	8.30	11.00	------
3	3.88	7.16	8.08	8.28	-----	------
4	3.89	7.18	8.04	8.33	11.15	9.53 (s_{br}, 1H,NH), 9.66 (s_{br}, 1H, NH)
5	3.88	7.16	8.07	8.27	9.25	----
6	3.79	7.01	7.38	-----	11.75	5.02 (d, 1H, C_5-H), 5.13 (d, C_6-H), 11.85 (s_{br}, 1H, NH)
7	3.87	7.14	8.06	8.26	-----	----
8	3.89	7.20	8.12	8.32	11.20	3.08 (s, 3H, N-CH_3), 10.42 (s_{br}, 1H, NH)
9	3.91	7.15	8.02	8.27	10.48	4.32 (t, 2H, CH_2), 5.27 (dd, 2H, CH=CH_2), 5.97(m, 1H, CH=CH_2), 9.00 (S_{br}, NH)
10	3.85	7.09	7.94	8.00	7.50	2.60 (t, 2H, CH_2), 3.00 (t, 2H, CH_2), 8.50 (s_{br}, 1H, OH)
11	3.88	6.98	8.00	8.17	8.45	3.51 (S, 3H, $COOCH_3$)
12	3.90 (6H)	7.00 (4H)	8.01 (4H)	8.41 (2H)	----	7.33 (dd, 2H, Ar-H), 7.63 (dd, 2H, Ar-H), 8.62 (s, 2H, NH_2)
13	3.88 (6H)	7.16 (4H)	8.25 (4H)	8.30 (2H)	9.84 (2H)	7.33 (dd, 2H, Ar-H), 7.66 (dd, 2H, Ar-H)
14	3.87	7.17	8.20	8.31	----	5.80 (s_{br}, 1H, NH), 7.39 (dd, 2H, Ar-H), 7.68 (dd, 2H, Ar-H)
15	3.89	7.16	8.06	8.31	----	6.92 (m, 3H, Ar-H), 7.94 (d, 1H, Ar-H), 9.18 (s_{br}, 1H, NH), 10.12 (s_{br}, 1H, NH)
16	3.90	----	8.05	8.40	8.35	5.45 (s, 1H, OH), 7.15 (m, 6H, Ar-H + C_2-H)
17a	3.91	7.00	8.07	8.31	----	7.31 (m, 5H, C_6H_5)
17b	3.92	7.03	8.10	8.35	----	7.37 (m, 4H, Ar-H)
17c	3.91	-----	8.06	8.30	----	2.37 (s, 3H, CH_3), 7.13 (m, 6H, Ar-H + C_2-H)

Solvent used is DMSO-d_6 except for **9**, **11**, **12** and **17a-c** is $CDCl_3$.

TABLE III

^{13}C-NMR data of prepared compounds



Compd. No.	C1	C2	C3	C4	C5	C6	C7	C8	C9	Others
2	55.62	161.19	115.17	131.50	124.16	154.14	100.16	116.32	164.18	165.12 (C=O)
3	55.97	162.05	115.18	133.52	124.20	154.15	100.02	117.31	--	163.89(O-C=N), 164.03 (C=O)
4	55.49	160.02	114.43	133.55	124.26	153.18	101.82	116.30	163.91	181.61 (C=S)
6	55.99	160.47	114.58	129.36	127.00	--	--	115.28	163.22	47.97(CH), 50.21(CH), 178.88 (C=S)
7	56.00	162.16	115.25	133.62	124.19	154.20	101.01	117.31	164.21	163.92(O-C=N), 180.60 (C=S)
8	55.01	162.17	115.20	133.48	124.91	153.21	102.31	117.00	165.16	54.38(CH_3), 182.15 (C=S)
9	55.81	161.20	115.16	134.29	124.05	155.54	98.20	116.11	165.00	48.21(CH_2), 117.84($CH=\underline{C}H_2$) 131.92($\underline{C}H=CH_2$) 179.66 (C=S)
10	55.72	162.05	114.82	132.12	125.58	149.13	108.31	119.15	164.74	32.25 (CH_2), 35.30 (CH_2CO), 172.77 (COOH)
11	55.66	162.43	114.86	133.78	124.82	154.71	99.33	116.57	164.10	57.20($COO\underline{C}H_3$), 163.92 ($\underline{C}OO$-)
15	55.94	159.41	115.19	133.08	125.71	156.49	102.41	117.45	163.24	151.49, 148.15, 125.82, 124.68, 122.23, 119.45 (Ar-C)
17a	55.72	162.05	114.99	134.19	126.39	155.88	98.31	116.35	164.32	121.41,129.61, 122.05, 152.3 (Ar-C)
17b	55.74	162.31	115.03	134.29	127.60	156.39	98.00	118.30	164.46	123.59, 124.31, 127.92, 130.54, 147.0 (Ar-C)
17c	55.71	162.23	114.99	134.07	124.78	155.76	98.81	116.21	164.31	20.9 (CH_3), 121.07, 130.10, 131.2,148.9 (Ar-C)

TABLE IV

Larvicidal activity of compounds prepared and conventional insecticides against Larvae of *CX. pipiens*

Compd. No.	LC 50 (ppm)	Relative potency
2	3.5	0.000004
5	11	0.000014
6	7	0.000021
7	2	0.000075
11	0.09	0.0016666
12	0.1	0.0015
14	15	0.00001
17a	39	0.000004
17b	13	0.000012
17c	3	0.00005
Permithren	0.00015	1

2,6-Bis[(2'-p-anisyl-1'-cyano)ethen-1'-yl]-1,3,5-oxadiazin-4-thione (7)

Procedure A: A mixture of **5** (1 g) and phosphoryl chloride (10 ml) was heated on a water-bath for 6 h. After cooling, the reaction mixture was poured into crushed ice (50 g) and the solid separated was filtered, washed with water (2 × 20 ml) dried and crystallized from toluene-ethanol mixture to give **7** as yellow crystals.

Procedure B: A mixture of **5** (1 g) and piperidine (3 drops) in ethanol (30 ml) was refluxed for 8 h. The solid separated after concentration was collected and crystallized from toluene-ethanol mixture to give **7** in 92% yield.

Conversion of **4** *into* **7**

The thiourea derivative (**4**) (0.5 g) was fused at 180–185°C for 2 h. After cooling the mass solid was crystallized from toluene-ethanol mixture to give **7** in 95% which identified by TLC, m.p., m.m.p. and spectral data.

N-(3-p-Anisyl-2-cyano-2-propenoyl)-N'-methylthiourea (8) *and* (5)

A mixture of **1c** or **1b** (0.01 mol) and methylthiourea (0.01 mol) in dry benzene (50 ml) was refluxed for 3 h. The solid separated was filtered and crystallized from toluene to give **5** in 72% yield which identified by m.p., m.m.p. and TLC. The filtrate was concentrated till dryness, triturated with diethyl ether and the residue was crystallized from petroleum-ether 60–80°C-benzene mixture to give **8** as yellow crystals.

N-Allyl-N'-(3-p-anisyl-2-cyano-2-propenoyl)thiourea (9)

A mixture of **1c** or **1b** (0.01 mol) and allylthiourea (0.01 mol) in dry benzene (50 ml) was refluxed for 10 h. The solvent was removed and the residue was crystallized from petroleum-ether 60–80°C to give **9** as yellow crystals.

β-*N-(3-p-Anisyl-2-cyano-2-propenoyl)alanine* (10)

A mixture of **1c** and or **1b** (0.01 mol) and *β*-alanine (0.01 mol) in dry benzene (50 ml) was refluxed for 2 h. The solid separated after concentration was filtered and crystallized from ethanol to give **10** as pale yellow crystals.

Methyl N-(3-p-anisyl-2-cyano-2-propenoyl)carbamate (11)

A mixture of **1c** or **1b** (0.01 mol) and methyl carbamate (0.01 mol) in dry benzene (50 ml) was refluxed for 12 h. The solvent was removed and the residue was crystallized from petroleum-ether 80–100°C to give **11** as pale yellow crystals. MS; m/z: M^+ (260, 7%), (231, 3%), (217, 100%), (202, 5%), (186, 77%), (158, 34%).

2-Amino-N,N-bis-(3-p-anisyl-2-cyano-2-propenoyl)aniline (12) *and N,N'-bis-(3-p-anisyl-2-cyano-2-propenoyl)phenylenediamine(o-)* (13)

A mixture of **1c** or **1b** (0.01 mol) and *o*-phenylenediamine (0.01 mol) in dry benzene (50 ml) was refluxed for 30 min. The solid separated was filtered and crystallized from toluene-ethanol mixture to give **13** as yellow crystals. The solid separated after concentration of the filtrate was collected and crystallized from methanol to give **12** as pale yellow crystals.

2-(2'-p-Anisyl-1'-cyano)ethen-1'-yl]1H-benzimidazole (14)

A mixture of **13** (1 g) and phosphoryl chloride (10 ml) was heated on a water-bath for 10 h. The mixture was added after cooling to crushed ice. The solid separated was filtered, washed with water (2 × 20 ml) dried and crystallized from toluene-ethanol mixture to give **14** as yellow crystals and 3-*p*-anisyl-2-cyano-2-propenoic acid[15] (**1a**) which identified by m.p., m.m.p. and spectral data. MS of **14** m/z: M+1 (276, 12%), M^+ (275, 53%), M−1 (274, 100%), M-CH_3 (260, 10%), M-OCH_3 (244, 4%), M-C_7H_6O (169, 6%).

2'-Aminophenyl 3-p-anisyl-2-cyano-2-propenoylate (15) *and 2-N-(3'-p-anisyl-2'-cyano-2'-propenoyl)aminophenol* (16)

A mixture of **1c** or **1b** (0.01 mol) and 2-aminophenol (0.01 mol) in dry benzene (50 ml) was refluxed for 8 h. The solvent was removed and the residue was triturated with chloroform. The insoluble part in chloroform was filtered and crystallized from ethanol to give **15** as brown crystals. The chloroform was concentrated and the solid separated was collected and crystallized from toluene-ethanol mixture to give **16** as yellow crystals. MS of **15**: m/z: M^+ (294, 36%), M-C_6H_5N (203, 66%), M-C_6H_6NO (186, 100%), (158, 36%).

Aryl 3-p-anisyl-2-cyano-2-propenoylate (**17a–c**)

A mixture of **1c** or **1b** (0.01 mol) and phenols, namely, phenol, *o*-chlorophenol and *p*-cresol (0.01 mol) in dry benzene (50 ml) was refluxed for 3–4 h. The solvent was removed and the residue crystallized from petroleum-ether 80–100°C to give (**17a–c**) as pale yellow crystals. MS of **17c**: m/z: M^+ (293, 23%), (203, 2%), (186, 100%), (158, 24%).

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