Decomposition of 2-Propenoyl Azide Derivatives. Synthesis and Larvicidal Activity of Novel Products

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Key Words: *2-Propenoyl azide; larvicides; pesticides; Culex pipiens*

Summary

Decomposition of 2-propenoyl azide (**1c**) with nitrogen, oxygen, and sulfur nucleophiles affords the azido displacement products. Ring closure of some of these products produces the heterocyclic systems pyrimidone (**3**), oxadiazine (**6**), oxadiazole (**8**), benzimidazole (**10**), benzothiazole (**12**), and benzoxazinone (**14**). The larvicidal activity of some of these products against *Culex pipiens* was evaluated.

Introduction

In keeping with the high level of interest shown[1–4] in the synthesis of some new acrylonitrile derivatives bearing heterocyclic moieties of characteristic pesticidal and insecticidal activities, such as pyrimidinethiones[5], oxadiazine[6], oxadiazoles[7,8],benzimidazoles[9,10], benzothiazoles[11], as well as diarylureas[12], this paper reports on the reactivity of (*E*)-2-cyano-3-(2′-thienyl)-2-propenoyl chloride (**1b**) and its azide (**1c**) towards some nitrogen, sulfur, and oxygen nucleophiles with the aim of studying 1) the mode of decomposition of acyl azide (**1c**) (azido or Curtius), 2) whether replacement of the anisyl moiety (as aromatic) by the thienyl moiety (as heterocycle) enhances the activity of the new acrylonitrile derivatives against larvae of *Culex pipiens* relative to values found in the previous study[1].

Decomposition of (*E*)-2-cyano-3-(2′-thienyl)-2-propenoyl azide (**1c**) with thiourea in toluene under reflux proceeded normally, involving not only mono-and di-displacement (**2** and **5**), but also the pyrimidinone derivative (**3**) as well as the imide derivative (**4**) (Scheme 1).

The formation of **3**, **4**, and/or **5** from the mono-displacement product (**2**) can be explained by addition of the free amino group of **2** to the double bond of the α,β-unsaturated nitrile to give **3**, while further nucleophilic displacement by the amino group of the intermediate amide [R-CO-NH_2] of **1c** or **2** with the elimination of (HN_3) and/or (NH_3) afforded **4** and **5**, respectively.

Ring closure of **5** on heating at 170 °C without solvent yielded the 1,3,5-oxadiazine-4-thione derivative (**6b**) (Scheme 1). Decomposition of azide (**1c**) with urea and/or thiourea at 170 °C afforded the 1,3,5-oxadiazin-4-one (thione) (**6a** and **6b**) by diazido displacement with subsequent cyclization (Scheme 1).

Acid hydrazides, namely, phenylacetic hydrazide and/or p-toluene-sulfonyl hydrazide reacted with azide (**1c**) to give the 2-propenoic hydrazide derivatives (**7a** and **7b**) (Scheme 1). Treatment of **7a** with phosphoryl chloride yielded the 1,3,4-oxadiazole derivative (**8**) (Scheme 1).

o-Phenylene diamine reacted with **1c** to give the di-displacement product, i.e. the *N*,*N*′-(dipropenoyl)-1,2-diaminobenzene derivative (**9**) (Scheme 2).

Cyclization of **9** upon treatment with phosphoryl chloride gave the intermediate (A), which hydrolyzed to give a mixture of 1H-benzimidazole (**10**) and acid (**1a**) (Scheme 2).

On the other hand, decomposition of azide (**1c**) with 2-aminothio-phenol yielded only the monosubstituted *S*-propenoylate derivative (**11**) (Scheme 2), which upon heating without solvent just at its melting point, underwent ring closure to give the 1,3-benzothiazole derivative (**12**) (Scheme 2).

Reaction of **1c** with anthranilic acid produced the *N*-propenoyl derivative (**13**) (Scheme 2). Treatment of **13** with acetic anhydride yielded the corresponding 3,1-benzoxazin-4-one derivative (**14**) (Scheme 2). Furthermore, decomposition of azide (**1c**) with 2-aminophenol gave a mixture of the expected mono- and di-displacement products **15** and **16,** respectively (Scheme 2). Similarly, decomposition of **1c** with alcohols or phenol yielded the alkyl and/or aryl 2-propenoylate derivatives (**17a–d**) in quantitative yields (Scheme 2).

In all of the previous reactions, the decomposition of the azide (**1c**) proceeds by an azido-displacement[1]; the same products were obtained from the reaction of the acid chloride (**1b**) with the same reagents.

Larvicidal Activity

Materials and Methods

The biological activity of 12 compounds against *Culex pipiens* larvae was determined using the WHO test technique[13]. *Culex pipiens* larvae used in this study were collected from Banha City, Quliubia Gov, Egypt. They were reared in an 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 h. Six different concentrations of the selected compounds were used in the bioassay tests. In each test, 25 mosquito larvae, put in glass jar with 250 ml tap water, were treated with the compounds.

Each test was replicated four times according to the standard testing procedure recommended by the WHO[13] (1975). The dead larvae were removed and mortality was calculated. Total percent mortality was corrected using Abbott's formula[14] (1925).

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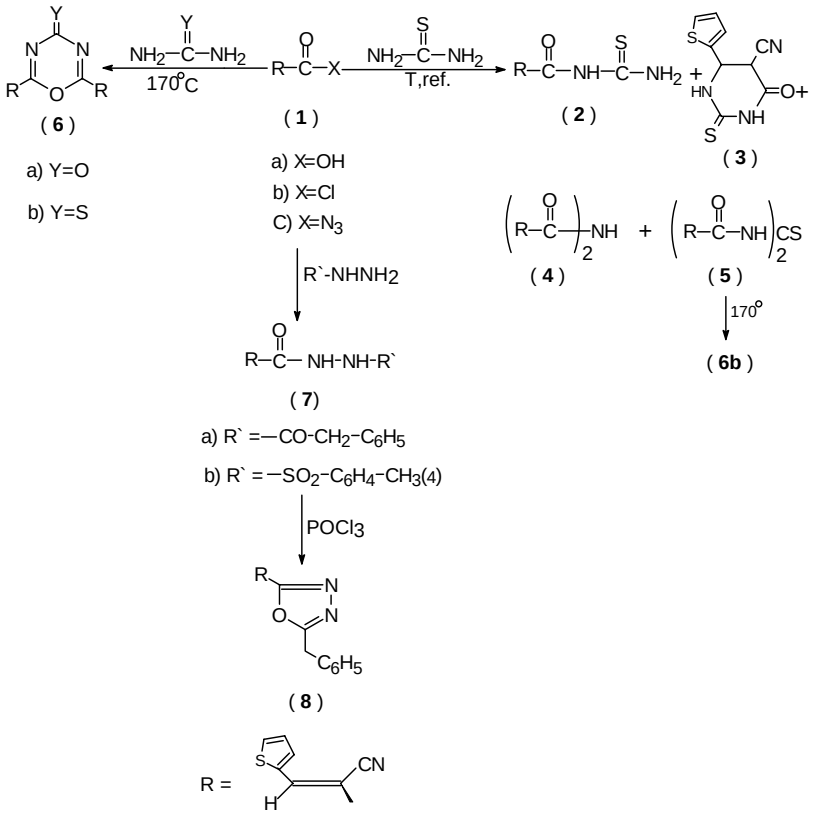
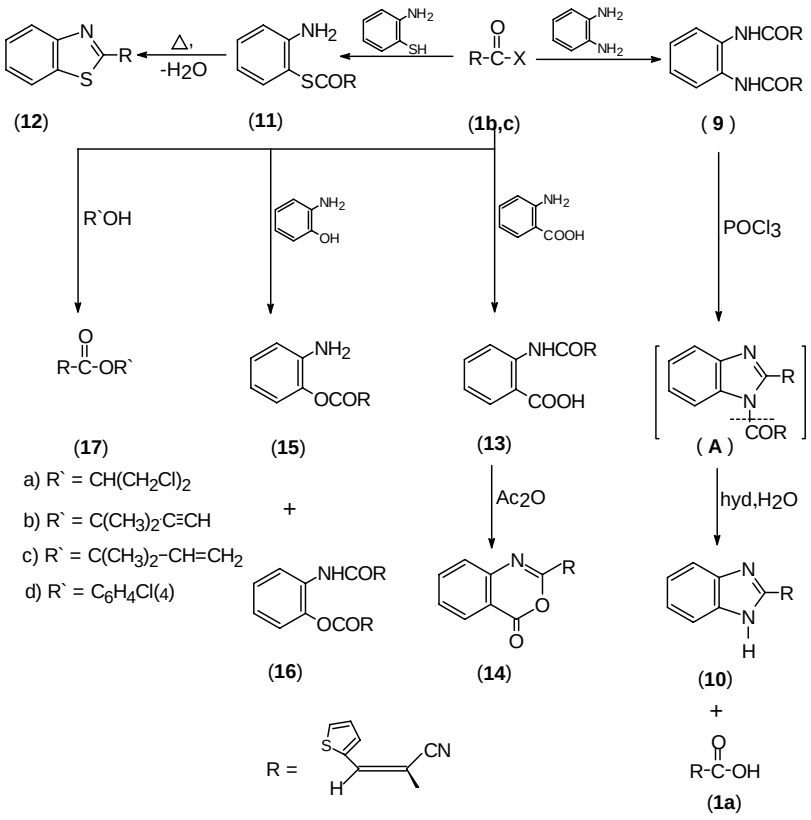


Scheme 1



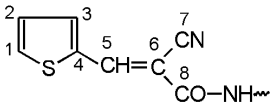
Scheme 2

Table 1: Data of compounds prepared.

Cpd. No.	Mp °C	IR NH,OH	IR C≡N	IR C=O	IR C=S	M. formula (MW) [a]
1b	105–106	2205	1740			C_8H_4ClNOS (197.65)
2	205–206	3359 3180	2215	1690	1137	$C_9H_7N_3OS_2$ (237.31)
3	196–198	3345	2205	1685	1130	$C_9H_7N_3OS_2$ (237.31)
4	189–190	3310	2215	1675	——	$C_{16}H_9N_3O_2S_2$ (339.39)
5	242–245	3280	2210	1670	1150	$C_{17}H_{10}N_4O_2S_3$ (398.47)
6a	315–318	——	2222	1685	——	$C_{17}H_8N_4O_2S_3$ (364.40)
6b	302–303	——	2216	——	1145	$C_{17}H_8N_4OS_3$ (380.46)
7a	180–182	3295 3265	2215 1658	1695	——	$C_{16}H_{13}N_3O_2S$ (311.36)
7b	182–183	3280	2220	1680	——	$C_{15}H_{13}N_3O_3S_2$ (347.42)
8	155–157	——	2218	——	——	$C_{16}H_{11}N_3OS$ (293.35)
9	233–236	3435	2211	1668	——	$C_{22}H_{14}N_4O_2S_2$ (430.51)
10	216–218	3485	2218	——	——	$C_{14}H_9N_3S$ (251.31)
11	210	3360 3320	2222	1686	——	$C_{14}H_{10}N_2OS_2$ (286.38)
12	182–184	——	2218	——	——	$C_{14}H_8N_2S_2$ (268.36)
13	252–255	3600 2750 (br)	2215 1660	1685	——	$C_{15}H_{10}N_2O_3S$ (298.32)
14	232–234	——	2210	1770	——	$C_{15}H_8N_2O_2S$ (280.31)
15	177–179	3480	2220	1740	——	$C_{14}H_{10}N_2O_2S$ (270.31)
16	190–192	3419 2220	2215 1695	1730	——	$C_{22}H_{13}N_3O_3S_2$ (431.50)
17a	103–104	——	2205	1740	——	$C_{11}H_9Cl_2NO_2S$ (290.18)
17b	140–141	——	2218	1730	——	$C_{13}H_{11}NO_2S$ (245.30)
17c	154–155	——	2215	1735	——	$C_{13}H_{13}NO_2S$ (247.32)
17d	173.5	——	2210	1735	——	$C_{14}H_8ClNO_2S$ (289.70)

[a] C,H,N analyses were ± 0.4% of calculated values.

Table 2: ^{13}C-NMR of prepared compounds.



Cpd.no.	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	Others
1b	129.59	139.13	140.56	135.44	149.99	100.51	114.91	163.30	———————-
2	128.81	135.56	139.49	137.43	146.07	99.01	116.19	163.43	188.02, (C=S)
3	128.46	135.75	139.46	136.08	———	———	116.30	163.06	177.50 (C=S),46.52 (CH), 51.20 (CH)
4	129.49	136.61	139.48	129.81	147.75	100.19	116.32	163.75	————————
7a	129.14	136.55	138.21	136.34	147.51	100.20	115.40	163.29	41.26 (CH_2),126.36 128.36,128.50, 139.34 (Ar-C).
7b	129.15	136.21	139.19	136.36	146.63	99.98	116.18	160.21	21.50 (CH_3),129.45, 130.33,136.95,145.97, (Ar-C).
8	128.56	136.28	138.37	135.48	144.81	98.98	116.01	———	39.94 (CH_2),126.36, 128.36,128.86,139.34, 160.56 (Ar-C).
9	128.75	135.81	138.42	135.66	144.63	101.68	116.47	160.34	125.91,130.79, (Ar-C).
10	128.53	135.44	139.08	135.30	146.95	100.20	115.40	———	128.66,128.80,139.31, (Ar-C),143.80 (C=N).
11	128.07	135.49	138.41	135.67	143.96	100.23	115.34	157.21	119.73,123.33,124.33, 127.26,131.16,136.16, 136.80 (Ar-C).
16	128.56 128.93	135.44 135.46	138.08 140.60	135.61 137.79	144.17 148.35	101.81 97.53	115.65 116.27	160.25 160.45	123.20,125.41,126.32, 129.21,137.79,142.47, (Ar-C).
17a	128.84	136.16	137.94	135.89	147.79	98.14	115.08	161.78	42.31 (CH_2),73.89 (CH)
17b	128.63	135.22	137.21	136.01	146.83	99.73	115.60	160.85	28.87 (CH_3),73.37 CH 74.24 (-C-), 83.72 (-C)
17c	128.60	137.08	137.47	136.08	146.15	100.59	113.74	161.21	26.34 (CH_3),63.34 (CH2). 83.65, (CH)
17d	128.93	136.45	138.21	131.90	148.39	98.50	115.35	163.50	122.71, 129.66, 139.95 (Ar-C).

Table 3: Larvicidal activity of prepared compounds and conventional insecticides against larvae of *Culex pipiens*.

Compound No.	LC 50 (ppm)	Relative potency
2	8	0.00002
3	15	0.00001
5	4	0.00004
6a	32	0.000005
6b	0.5	0.0003
8	42	0.000004
10	11	0.000014
12	18	0.000008
14	22	0.000007
15	38	0.000004
17a	2	0.00008
17d	12	0.000013
Permithren	0.00015	1

The results listed in Table 3 show the relative toxicity of 12 compounds. The most effective compounds are nos. **6b**, **17a,** and **5**. Apparently, the thienyl moiety is not always a good mimic of aryl moieties.

Acknowledgment

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Experimental

All melting points are uncorrected. IR spectra are measured on a Pye Unicam SP 200G spectrometer by the KBr wafer technique. ^{1}H-NMR and ^{13}C-NMR spectra determined on a Bruker AC-250 and Bruker AMX-400 spectrometer. All chemical shifts (δ) are expressed in ppm. Mass spectra were determined on a Finnigan-MAT-311 A mass spectrometer (70 eV).

*2-Cyano-3-(2′-thienyl)-2-propenoyl chloride (**1b**)*

A mixture of acid[15] (**1a**) (5g) and thionyl chloride (20 mL) was heated on a water bath for 6 h. Excess thionyl chloride was distilled off until dryness; the residue was collected and washed with petroleum ether 40–60 °C to give **1b** as yellow crystals in 89% yield.– ^{1}H-NMR ($CDCl_3$) of **1b**:7.34 (t,1H,2-H), 8.00 (d,1H,1-H), 8.08 (d,1H,3-H), 8.48 (s,1H,4-H). MS of **1b**: *m/z*: M^+ (197, 42%), M + 2 (199, 6%), 162 (100%), 134 (42%), 107 (47%), 84 (9%).

*2-Cyano-3-(2′-thienyl)-2-propenoyl azide (**1c**)*

To a solution of **1b** (0.01 mol) in dry acetone (50 ml) was added portion-wise at 0 °C a sodium azide (0.02 mol) suspension in water (5 ml). After complete addition, the reaction mixture was stirred for a further 30 min and then poured onto cold water (50 ml). The precipitated solid was filtered off, washed with cold water (2×5 ml), and dried under reduced pressure to give **1c** (without crystallization) as yellow solid in 88% yield, mp 82 °C (de-comp.).

*N-[2-Cyano-3-(2′-thienyl)-2-propenoyl]thiourea (2),5-cyano-6-(2′-thienyl)-2-thioxo-hexahydropyrimidin-4-one (**3**), bis[2-cyano-3-(2′-thienyl)-2-propenoyl]amine (**4**) and N,N′-bis[2-cyano-3-(2′-thienyl)-2-propenoyl]-thiourea (**5**)*

A mixture of **1c** or **1b** (0.01 mol) and thiourea (0.01 mol) in toluene (50 mL) was refluxed for 30 min. The separated solid was filtered off and re-crystallized from ethanol to give **2** as yellow crystals in 30% yield. The solid precipitated on concentration of the filtrate was collected and triturated with a toluene/petroleum ether (60–80 °C) mixture and toluene to give **3** as yellow crystals in 15% yield, **4** as yellow crystals in 5% yield, and **5** as yellow crystals in 9% yield.

^{1}H-NMR (DMSO-d_6) of **2**:7.33 (t,1H,2-H), 7.82 (d,1H,1-H), 8.02 (d,1H,3-H), 8.42 (s,1H,4-H),8.80 (s_{br},1H,NH), 9.12 (s_{br},1H,NH), 9.82 (s_{br},1H,NH).

MS of **2**: *m/z*: M^+ (237, 8%), $[M–1]^+$ (236,11%), 204 (3%), 179 (78%), 162 (100%), 134 (83%), 58 (42%).

^{1}H-NMR (DMSO-d_6) of **3:** 5.30 (d,1H,CH), 5.65 (d,1H,CH), 7.22 (t,1H,2-H), 7.82 (d,1H,1-H), 8.05 (d,1H,3-H), 11.10 (s_{br},1H,NH), 11.50 (s_{br},1H-NH).

MS of **3**: *m/z*: M^+ (237, 18%), $[M\text{-}SH]^+$ (204, 12%) 192 (4%), 178 (12%), 162 (100%), 134 (50%), 108 (16%), 91 (55%).

^{1}H-NMR (acetone-d_6) of **4:** 7.35 (t,1H,2-H), 7.38 (t,1H,2-H), 7.83 (d,1H,1-H), 7.92 (d,1H,1-H), 8.03 (d,1H,3-H), 8.09 (d,1H,3-H), 8.45 (s,1H,4-H), 8.49 (s, 1H,4-H), 9.55 (s_{br},1H,NH).

MS of **4**: *m/z*: $M^{\cdot+}$ (339, 15%), $[M\text{-}1]^+$ (338,12%), 298 (3%), 205 (2%), 191 (10%), 177 (12%), 162 (100%), 134 (65%), 97 (99%), 84 (10%).

*2,6-Bis[(2′-thienyl-1′-cyano)-ethene-1′-yl]-1,3,5-oxadiazin-4-one (thione) (**6a** and **b**)*

A mixture of **1c** or **1b** (0.01 mol) and urea or thiourea (0.01 mol) was heated at 170 °C without solvent for 2h. After cooling the solid was triturated with ethanol, the solid separated was filtered, washed with ethanol and crystallized from toluene to give **6a** and **6b** as brown crystals in 86% and 65% yield respectively.

*Conversion of **5** into **6b***

The solid compound **5** (1g) was heated without solvent at 170 °C for 30 min. After cooling, the solid was triturated with toluene under reflux and filtered. The solid separated from filtrate, was collected and identified as **6b** (96% yield) by mp, m. mp, TLC, and spectral data.

*N-(Phenylacetyl and/ or p-toluenesulfonyl)-2-cyano-3-(2′-thienyl)-2-propenoic hydrazides (**7a** and **b**)*

A mixture of **1c** or **1b** (0.01 mol), acid hydrazides, namely, phenylacetic hydrazide and/or p-toluene sulfonyl hydrazide (0.01 mol) and triethylamine (0.01 mol) in toluene (50 mL) was refluxed for 30 min. The solvent was removed and the residue was triturated with cold dilute hydrochloric acid (20 mL, 10%). The solid produced was collected, washed with water (2×10 mL), dried, and crystallized from ethanol to give **7a** and **b** as colourless crystals in 65 and 90% yield respectively.

^{1}H-NMR (acetone-d_6) of **7a:** 2.77 (s,2H,CH_2), 7.35 (m,7H,2-H+NH+Ar-H), 7.95 (d,1H,1-H), 8.08 (d,1H,3-H), 8.50 (s,1H,4-H), 9.45 (s_{br},1H,NH).

MS of **7a** *m/z*: $[M+1]^+$ 312 (3%), 225 (5%), 193 (3%), 162 (30%), 134 (12%), 118 (42%), 91 (100%).

^{1}H-NMR ($CDCl_3$) of **7b:** 2.4 (s,3H,CH_3), 7.30 (m,5H,2-H+Ar-H), 7.75 (d,1H, 1-H), 7.82 (d,1H,3-H), 7.90 (s_{br},1H,NH), 8.20 (s,1H,4-H), 8.39 (s_{br},1H,NH).

MS of **7b**: *m/z*: $M^{\cdot+}$ (347, 3%), 192 (10%), 162 (100%), 84 (38%).

2-Benzyl-5-([1′-cyano-2′-(2″-thienyl)]-ethen-1′-yl)-1,3,4-oxadiazole **(8)**

A mixture of **7a** (1g) and phosphoryl chloride (10 mL) was heated on a water bath for 2 h. After cooling, the reaction mixture was added to crushed ice (50g). The precipitated solid was collected, washed with water (2×20 mL), dried, and re-crystallized from chloroform to give **8** as red crystals in 70% yield.

^{1}H-NMR (DMSO-d_6) of **8:** 2.20 (s,2H,CH_2), 7.05 (m,6H,2-H+Ar-H), 7.77 (d, 1H,1-H), 7.83 (d,1H,3-H), 8.33 (s,1H,4-H).

MS of **8**: *m/z*: $M^{\bullet+}$ (293,2%), $[M–1]^+$ (292, 12%), 220 (8%), 193 (13%), 162 (28%), 134 (12%), 118 (40%), 91 (100%).

*N,N′-Bis[2-cyano-3-(2′-thienyl)-2-propenoyl]-1,2-diaminobenzene (**9**)*

A mixture of **1c** or **1b** (0.01 mol) and o-phenylene diamine (0.01 mol) in toluene (50 mL) was refluxed for 30 min. The solid precipitated during refluxing was collected and crystallized from toluene/ ethanol mixture to give **9** as yellow crystals in 72% yield.

^{1}H-NMR (DMSO-d_6) of **9:** 7.52 (m,4H,Ar-H), 7.82 (t,2H,2×2-H), 8.17 (d,2H, 2×1-H), 8.32 (d,2H,2×3-H), 8.80 (s,2H,2×4-H), 10.00 (s_{br},2H,2×NH).

MS of **9**: *m/z*: $M^{\bullet+}$ (430,10%), 268 (18%), 250 (19%), 225 (2%),162 (100%), 134 (44%), 90 (11%).

*2-([1′-cyano-2′-(2″-thienyl)]ethen-1′-yl)-1H-benzimidazole (**10**)*

A mixture of **9** (1 g) and phosphoryl chloride (10 mL) was heated on a water bath for 4 h. The mixture was added after cooling to crushed ice (50 g).The precipitated solid was filtered off, washed with water (2×10 mL), dried, and crystallized from toluene to give **10** as yellow crystals in 52% yield, the insoluble residue was crystallized from ethanol to give **1a** which identified by mp, m. mp, and spectral data.

^{1}H-NMR ($CDCl_3$) of **10:** 7.38 (m,4H,Ar-H), 7.90 (t,1H,2-H), 8.10 (d,1H,1-H), 8.18 (d,1H,3-H), 8.35 (s,1H,4-H), 8.92 (s,1H,NH).

*S-(2′-Aminophenyl)2-cyano-3-(2″-thienyl)-2-thiopropenoylate (**11**)*

A mixture of **1c** or **1b** (0.01 mol) and 2-aminothiophenol (0.01 mol) in toluene (50 mL) was refluxed for 1 h. The solid separated during reflux was collected and identified as aminothiophenol hydrochloride. The filtrate was concentrated and the precipitated solid was collected and crystallized from a petroleum-ether (60–80 °C)/toluene mixture to give **11** as yellow crystals in 25% yield.

^{1}H-NMR ($CDCl_3$) of **11:** 7.05 (t,1H,Ar-H), 7.22 (d,1H,Ar-H), 7.35 (m,2H,2-H+Ar-H), 7.51 (d,1H,Ar-H), 7.84 (d,1H,3-H), 7.82 (d,1H,1-H), 8.39 (s,1H, 4-H), 8.45 (s_{br},1H,NH), 9.10 (s,1H,NH).

MS of **11**: *m/z*: M^+ (268, 2%), $[M–1]^+$ (289, 20%), 268 (4%), 267 (19%), 242 (20%), 162 (100%), 150 (20%), 134 (55%).

*2-([1′-Cyano-2′-(2″-thienyl)]-ethen-1′-yl)-1,3-benzothiazole (**12**)*

Thio ester **11** (1 g) was heated without solvent at 210 °C for 2 h. The mass residue was crystallized from toluene to give **12** as yellow crystals in 85% yield. MS of **12**: *m/z*: $M^{\bullet+}$ (268, 23%), $[M–1]^+$ 268 (100%), 134 (75%), 108 (40%), 82 (34%).

*N-[2-Cyano-3-(2′-thienyl)-2-propenoyl] anthranilic acid (**13**)*

A mixture of **1c** or **1b** (0.01 mol) and anthranilic acid (0.01 mol) in toluene (50 mL) was refluxed for 1 h. The solid precipitated during refluxing was filtered off and crystallized from ethanol to give **13** as yellow crystals in 88% yield. MS of **13**: *m/z*: $M^{\bullet+}$ (298, 6%), 280 (60%), 254 (35%), 177 (22%), 162 (100%), 136 (72%), 91 (53%).

*2-([1′-Cyano-2′-(2″-thienyl)]-ethen-1′-yl)-3,1-benzoxazin-4-one (**14**)*

Compound **13** (1 g) in acetic anhydride (5 mL) was heated on a water bath for 30 min. The reaction mixture was poured onto crushed ice (30 g). The precipitated solid was filtered off, washed with water (2×10 mL), dried, and crystallized from an ethanol/acetic acid mixture to give **14** as yellow crystals in 97% yield.

*2′-Aminophenyl 2-cyano-3-(2″-thienyl)-2-propenoylate (**15**) and 2′-[N-(2″-cyano-3″-(2‴-thienyl)-2′-propenoyl)]aminophenyl 2-cyano-3-(2′-thienyl)-2-propenoylate (**16**)*

A mixture of **1c** or **1b** (0.01 mol) and 2-aminophenol (0.01 mol) in toluene (50 mL) was refluxed for 30 min. The solid separated immediately was collected and crystallized from toluene/ethanol mixture to give **16** as yellow crystals in 35% yield, the filtrate was concentrated and the precipitated solid was collected and crystallized from toluene to give **15** as yellow crystals in 12% yield.

^{1}H-NMR (acetone-d_6) of **15:** 7.25 (m,5H,2-H+Ar-H), 8.00 (m,3H,1-H+3-H+ NH), 8.44 (s,1H,4-H), 8.80 (s_{br},1H,NH).

MS of **15**: *m/z*: $M^{\bullet+}$ not detected, 253 (3%), 251 (25%), 162 (100%), 134 (48%), 108 (10%), 91 (46%).

^{1}H-NMR (DMSO-d_6) of **16:** 7.50 (m,6H,2×2-H+Ar-H), 8.06 (d,1H,1-H), 8.25 (d,1H,1-H), 8.29 (d,1H,3-H), 8.40 (d,1H,3-H), 8.62 (s,1H,4-H), 8.95 (s,1H,4-H), 10.22 (s_{br},1H,NH).

MS of **16**: *m/z*: $M^{\bullet+}$ (431, 5%), 296 (3%), 270 (6%), 252 (25%), 11 (18%), 162 (100%), 134 (38%), 90 (12%).

*Alkyl and/or Aryl 2-cyano-3-(2′-thienyl)-2-propenoylates (**17a-d**)*

General procedure:

A mixture of **1c** or **1b** (0.01 mol), alcohols and/or phenols, *viz.* 1,3-dichloro-2-propanol, 2-methyl-3-butyn-2-ol, 2-methyl-3-buten-2-ol, and/or p-chlorophenol (0.01 mol), respectively and triethylamine (0.01 mol) in toluene (30 mL) was refluxed for 2–4 h. The solvent was removed and the residue was neutralized with cold dilute hydrochloric acid (20 mL, 10%). The precipiated solid was collected, washed with water (2×10 mL), dried and crystallized from petroleum-ether 60–80 °C to give **17a–c** as yellow crystals in 92–95% yield and **17d** as brown crystals in 60% yield.

^{1}H-NMR ($CDCl_3$) of **17a:** 3.85 (d,4H,2×CH_2), 5.32 (t,1H,CH), 7.29 (t, 1H, 2-H), 7.85 (d,1H,1-H), 7.90 (d,1H,3-H), 8.46 (s,1H,4-H).

MS of **17a**: *m/z*: $M^{\bullet+}$ (290, 10%), 179 (98%), 162 (100%), 134 (43%), 108 (10 %);

^{1}H-NMR ($CDCl_3$) of **17b:** 1.80 (s,6H,2×CH_3), 2.62 (s,1H,CH), 7.23 (t,1H, 2-H) 7.80 (d,1H,1-H), 7.81 (d,1H,3-H), 8.39 (s,1H,4-H).

MS of **17b**: *m/z*: $M^{\bullet+}$ (245, 40%), 179 (100%), 162 (80%), 134 (39%), 108 (12%).

^{1}H-NMR ($CDCl_3$) of **17c:** 1.60 (s,6H,2×CH_3), 5.15 (d,1H,CH_2), 5.30 (d,1H, CH_2), 6.15 (dd,1H,CH), 7.35 (t,1H,2-H), 7.75 (d,1H,1-H), 7.80 (d,1H,3-H), 8.38 (s,1H,4-H).

MS of **17c**: *m/z*: $M^{\bullet+}$ (247, 22%), 179 (42%), 162 (25%), 134 (8%), 108 (9%), 69 (100%).

^{1}H-NMR ($CDCl_3$) of **17d:**7.15 (d,2H,Ar-H),7.42 (d,2H,Ar-H), 7.35 (t,1H,2-H), 7.82 (d,1H,1-H), 7.92 (d,1H,3-H), 8.50 (s,1H,4-H).

MS of **17d**: *m/z*: $M^{\bullet+}$ (289, 3%), 179 (12%), 162 (100%), 134 (38%), 108 (5%), 84 (3%).

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