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Novel 2-alkylthio-5-furylmethylidene-4*H*-imidazolin-4-ones **4** have been synthesized *via* tandem aza-Wittig reaction. The structures were determined by ir, nmr, mass spectroscopy, and elemental analysis. They were screened for fungicidal activities against *Fusarium oxysporium*, *Botryosphaeria berengeriana* and *Rhizoctonia solani*, and growth inhibition of Barnyard grass and Cole root and stalk. A few of them possess significant biological activities.

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Introduction.

4*H*-Imidazolin-4-ones derivatives are found to possess significant biological activities such as fungicidal and herbicidal activities. They are highly important heterocycles, and have been one of the most successfully used in research and development of agrochemicals [1-5]. Since a novel mitochondrial respiratory inhibitor, 5-methyl-2-methylthio-5-phenyl-3-phenylamino-3,5-dihydro-imidazolin-4-one, was found to show high fungicidal activity,

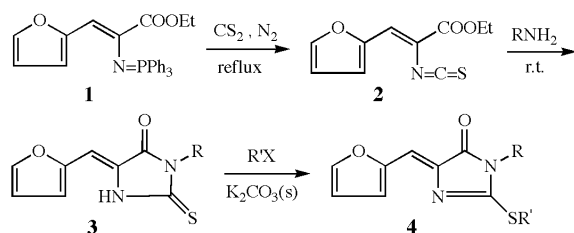
many other 2-methylthio-imidazolinone derivatives have been synthesized to evaluate their fungicidal activities [6-10]. Most of those reported are 5,5-dialkyl-substituted 2-methylthio-imidazolinones synthesized from the corresponding amino acetic acid [7,9]. However, 2-alkylthio-5-furylmethylidene-imidazolinones can not be synthesized *via* the general method because of the unstable starting material, vinyl amino acetic acid. As part of our current studies on the synthesis of the biologically active imida-

Table 1
Synthesis of Compounds **2**, **3a - k** and **4a - t**

No.	R	R' X	Reaction Conditions [a]	Yield [b] (%)
2	/	/	75 °C / 29 h	46
3a	Pr ⁿ	/	r.t. / 0.5 h	51
3b	Bu ⁿ	/	r.t. / 0.5 h	47
3c	Thenyl	/	r.t. / 1.5 h	57
3d	4-Morpholinoethylene	/	r.t. / 1 h	90
3e	2-Pyridylmethylene	/	r.t. / 0.5 h	64
3f	3-Pyridylmethylene	/	r.t. / 2 h	49
3g	2-F-Benzyl	/	r.t. / 3 h	60
3h	3-F-Benzyl	/	r.t. / 2 h	56
3i	4-F-Benzyl	/	r.t. / 2 h	58
3j	2-Cl-Benzyl	/	r.t. / 3 h	46
3k	3-Cl-Benzyl	/	r.t. / 3 h	61
4a	Pr ⁿ	Pr ⁿ Br	40 °C / 3 h	48
4b	Pr ⁿ	ClCH ₂ COOEt	60 °C / 5 h	54
4c	Bu ⁿ	MeI	r.t. / 1 h	69
4d	Thenyl	Bu ⁿ Br	50 °C / 5 h	30
4e	Thenyl	ClCH ₂ COOEt	60 °C / 5 h	47
4f	4-Morpholinoethylene	MeI	r.t. / 3 h	78
4g	4-Morpholinoethylene	ClCH ₂ COOEt	60 °C / 3 h	76
4h	2-Pyridylmethylene	MeI	r.t. / 3 h	64
4i	2-Pyridylmethylene	ClCH(Me)COOEt	60 °C / 3 h	81
4j	3-Pyridylmethylene	MeI	r.t. / 3 h	62
4k	2-F-Benzyl	MeI	r.t. / 3 h	87
4l	2-F-Benzyl	ClCH ₂ COOEt	60 °C / 5 h	93
4m	3-F-Benzyl	MeI	r.t. / 3 h	81
4n	3-F-Benzyl	ClCH ₂ COOEt	60 °C / 4 h	75
4o	4-F-Benzyl	MeI	r.t. / 1 h	51
4p	4-F-Benzyl	ClCH ₂ COOEt	60 °C / 3 h	59
4q	2-Cl-Benzyl	MeI	r.t. / 3 h	81
4r	2-Cl-Benzyl	ClCH ₂ COOEt	60 °C / 5 h	61
4s	3-Cl-Benzyl	MeI	r.t. / 1 h	89
4t	3-Cl-Benzyl	ClCH ₂ COOEt	60 °C / 2 h	73

[a] r.t.: room temperature; h: hour; [b] Isolated yields of **2** based on **1** used; Isolated yields of **3** based on **2** used; Isolated yields of **4** based on **3** used.

Scheme 1



zolinone derivatives *via* tandem aza-Wittig reaction [11-16], we now report the synthesis and biological activities of some novel 2-alkylthio-5-furylmethylidene-imidazolidinones (**4a-t**) from the stable vinyliminophosphorane **1**.

Results and Discussion.

The synthetic route (Scheme 1) involved the aza-Wittig reaction of the vinyliminophosphorane **1** with carbon

disulfide in refluxing dichloromethane for 29 hours at 75 °C under inert and anhydrous conditions, to obtain 3-furan-2-yl-2-isothiocyanato acrylic acid ethyl ester **2**. Cyclocondensation of the intermediate **2** *in situ* with RNH_2 at room temperature in 0.5 - 3 hours yielded directly 5-furylmethylidene-2-thio-4-imidazolidinones **3**.

Scheme 2

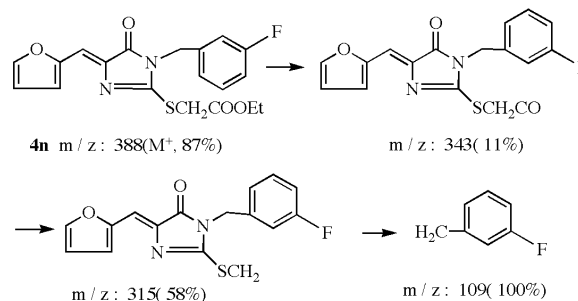


Table 2
Physical Properties and Elemental Analysis Data of Compounds **2**, **3a-k** and **4a-t**

No.	MF (MW)	Physical state	mp [c] (°C)	Found (Calcd.) (%)		
				C	H	N
2	C ₁₀ H ₉ NO ₃ S (223)	Brown crystals	42 - 43	53.92 (53.80)	4.00 (4.06)	6.36 (6.27)
3a	C ₁₁ H ₁₂ N ₂ O ₂ S (236)	Brown crystals	123 - 125	55.96 (55.91)	5.09 (5.12)	11.87 (11.86)
3b	C ₁₂ H ₁₄ N ₂ O ₂ S (250)	Yellow crystals	112 - 113	57.54 (57.58)	5.61 (5.64)	11.21 (11.19)
3c	C ₁₃ H ₁₀ N ₂ O ₂ S ₂ (290)	Brown crystals	240 - 241	53.78 (53.77)	3.45 (3.47)	9.68 (9.65)
3d	C ₁₄ H ₁₇ N ₃ O ₃ S (307)	Yellow crystals	173 - 175	54.68 (54.71)	5.59 (5.57)	13.69 (13.67)
3e	C ₁₄ H ₁₁ N ₃ O ₂ S (285)	Brown crystals	186 - 187	58.90 (58.93)	3.79 (3.89)	14.86 (14.73)
3f	C ₁₄ H ₁₁ N ₃ O ₂ S (285)	Yellow crystals	216 - 218	59.06 (58.93)	3.84 (3.89)	14.77 (14.73)
3g	C ₁₅ H ₁₁ FN ₂ O ₂ S (302)	Brown crystals	212 - 213	59.60 (59.59)	3.66 (3.67)	9.29 (9.27)
3h	C ₁₅ H ₁₁ FN ₂ O ₂ S (302)	Brown crystals	215 - 217	59.61 (59.59)	3.68 (3.67)	9.25 (9.27)
3i	C ₁₅ H ₁₁ FN ₂ O ₂ S (302)	Yellow crystals	197 - 198	59.58 (59.59)	3.70 (3.67)	9.26 (9.27)
3j	C ₁₅ H ₁₁ ClN ₂ O ₂ S (319)	Brown crystals	195 - 197	56.54 (56.52)	3.46 (3.48)	8.81 (8.79)
3k	C ₁₅ H ₁₁ ClN ₂ O ₂ S (319)	Brown crystals	196 - 198	56.49 (56.52)	3.49 (3.48)	8.77 (8.79)
4a	C ₁₄ H ₁₈ N ₂ O ₂ S (278)	Yellow crystals	89 - 90	60.44 (60.41)	6.55 (6.52)	10.01 (10.06)
4b	C ₁₅ H ₁₈ N ₂ O ₄ S (322)	Yellow crystals	80 - 81	55.70 (55.88)	5.28 (5.63)	8.79 (8.69)
4c	C ₁₃ H ₁₆ N ₂ O ₂ S (264)	Yellow crystals	95 - 97	59.04 (59.07)	6.13 (6.10)	10.12 (10.60)
4d	C ₁₇ H ₁₈ N ₂ O ₂ S ₂ (346)	Yellow solid	81 - 82	58.96 (58.93)	5.21 (5.24)	8.11 (8.09)
4e	C ₁₇ H ₁₆ N ₂ O ₄ S ₂ (376)	Brown solid	98 - 100	54.28 (54.24)	4.31 (4.28)	7.42 (7.44)
4f	C ₁₅ H ₁₉ N ₃ O ₃ S (321)	Yellow crystals	90 - 92	56.10 (56.06)	6.01 (5.96)	13.04 (13.07)
4g	C ₁₈ H ₂₃ N ₃ O ₅ S (393)	Yellow solid	110 - 111	55.00 (54.95)	5.91 (5.89)	10.65 (10.68)
4h	C ₁₅ H ₁₃ N ₃ O ₂ S (299)	Brown solid	130 - 132	60.19 (60.18)	4.40 (4.38)	14.00 (14.04)

Table 2 (continued)

No.	MF (MW)	Physical state	mp [c] (°C)	Found (Calcd.) (%)		
				C	H	N
4i	C ₁₉ H ₁₉ N ₃ O ₄ S (385)	Orange crystals	82 - 84	59.17 (59.21)	5.00 (4.97)	10.89 (10.90)
4j	C ₁₅ H ₁₃ N ₃ O ₂ S (299)	Brown solid	128 - 129	60.20 (60.18)	4.36 (4.38)	14.06 (14.04)
4k	C ₁₆ H ₁₃ FN ₂ O ₂ S (316)	Yellow solid	139 - 140	60.35 (60.75)	4.13 (4.14)	6.50 (6.01)
4l	C ₁₉ H ₁₇ FN ₂ O ₄ S (388)	Yellow solid	137 - 138	58.72 (58.75)	4.45 (4.41)	7.23 (7.21)
4m	C ₁₆ H ₁₃ FN ₂ O ₂ S (316)	Orange crystals	140 - 142	60.79 (60.75)	4.11 (4.14)	8.90 (8.86)
4n	C ₁₉ H ₁₇ FN ₂ O ₄ S (388)	Yellow crystals	98 - 100	58.77 (58.75)	4.44 (4.41)	7.20 (7.21)
4o	C ₁₆ H ₁₃ FN ₂ O ₂ S (316)	Yellow solid	131 - 132	60.80 (60.75)	4.15 (4.14)	8.82 (8.86)
4p	C ₁₉ H ₁₇ FN ₂ O ₄ S (388)	Orange crystals	133 - 135	58.71 (58.75)	4.43 (4.41)	7.25 (7.21)
4q	C ₁₆ H ₁₃ ClN ₂ O ₂ S (333)	Brown crystals	169 - 170	57.70 (57.74)	4.00 (3.94)	8.46 (8.42)
4r	C ₁₉ H ₁₇ ClN ₂ O ₄ S (405)	Brown solid	153 - 154	56.36 (56.36)	4.25 (4.23)	6.91 (6.92)
4s	C ₁₆ H ₁₃ ClN ₂ O ₂ S (333)	Brown crystals	142 - 143	57.73 (57.74)	3.90 (3.94)	8.44 (8.42)
4t	C ₁₉ H ₁₇ ClN ₂ O ₄ S (405)	Yellow solid	110 - 112	56.39 (56.36)	4.28 (4.23)	6.88 (6.92)

[c] Uncorrected.

Table 3
IR (KBr, ν/cm^{-1}), and EI-MS Data of Compounds **3a - k**, and **2**

No.	$\nu_{\text{N-H}}$	$\nu_{\text{C=O}}$	$\nu_{\text{C=C}}$	$\nu_{\text{C=C (in ring)}}$	$\nu_{\text{C=S}}$	m/z (abundance, %)
3a	3234;	1724;	1650;	1486, 1458, 1434, 1405;	1117	236(M ⁺ , 38); 194(23); 107(100)
3b	3293;	1735;	1652;	1485, 1455, 1442, 1403;	1129	250(M ⁺ , 44); 217(78); 107(100)
3c	3289;	1715;	1647;	1484, 1448, 1424, 1395;	1125	290(M ⁺ , 64); 257(45); 97(100)
3d	3235;	1730;	1650;	1485, 1453, 1447, 1407;	1115	307(M ⁺ , 11); 274(27); 100(100)
3e	3242;	1731;	1655;	1484, 1452, 1438, 1396;	1140	285(M ⁺ , 90); 252(75); 107(100)
3f	3120;	1716;	1649;	1498, 1466, 1431, 1399;	1143	285(M ⁺ , 90); 252(70); 107(100)
3g	3253;	1740;	1650;	1485, 1455, 1435, 1402;	1138	302(M ⁺ , 70); 269(11); 109(100)
3h	3292;	1737;	1651;	1484, 1449, 1433, 1399;	1139	302(M ⁺ , 82); 269(17); 109(100)
3i	3236;	1727;	1653;	1485, 1453, 1431, 1395;	1160	302(M ⁺ , 81); 269(12); 109(100)
3j	3230;	1726;	1648;	1483, 1447, 1436, 1395;	1149	320(M ⁺ +1,31); 318(M ⁺ -1,18); 107(100)
3k	3308;	1736;	1650;	1483, 1447, 1432, 1394;	1137	320(M ⁺ +1,35); 318(M ⁺ -1,93); 107(100)
2	2021(N=C=S); 1719(C=O); 1623(C=C); 1263(C=S)					223(M ⁺ ,100); 108(26); 45(39)

In the presence of K₂CO₃ (s), the S-alkylation reaction of **3** with R'X (X = Cl, Br, I) provided 2-alkylthio-5-furyl-methylidene-4*H*-imidazolin-4-ones **4** in satisfactory yields. When X was I or Br, the S-alkylation reaction could be carried out smoothly in 1 - 3 hours at room temperature; When X was Cl, reaction time was for 3 - 5 hours at 40 - 60 °C to accomplish the S-alkylation reaction. The presence of K₂CO₃ (s), **3**:K₂CO₃ (s) = 1:6-10 mole ratio, was necessary for the S-alkylation reaction to take place in short time and at lower temperature. Thin layer chromatography was employed to follow the progress of the above reactions.

All of the compounds **2**, **3a - k** and **4a - t** were readily soluble in polar organic solvents and melt within the 42 -

241 °C range. Reaction conditions and yields data are given in Table 1.

The structures of all compounds **2**, **3a - k** and **4a - t** were established on the basis of elemental analysis and spectral data. Physical properties and elemental analysis data of compounds **2**, **3a - k** and **4a - t** are presented in Table 2. The difference between found value and calculated value of elemental analysis of all compounds **2**, **3a - k** and **4a - t** was under 0.5 %.

The ir spectral data of the reaction products **2**, **3a - k** and **4a - t** are given in Table 3 and Table 4, and are in agreement with the corresponding structures [17]. The ir spectral data of compounds **2** showed absorption bands at 2021 cm⁻¹ due to N=C=S group, at 1719 cm⁻¹ due to C=O group, at 1623

Table 4
IR (KBr, ν/cm^{-1}), and EI-MS Data of Compounds **4a** – **t**

No.	$\nu_{\text{CO}_2\text{Et}}$	$\nu_{\text{C=O}}$	$\nu_{\text{C=C}}$	$\nu_{\text{C=N \& C=C}}$ (in ring)	m/z (abundance, %)
4a		1700;	1638;	1488, 1468	278(M^+ , 86); 236(90); 107(100)
4b	1729;	1708;	1639;	1491, 1466	322(M^+ , 100); 236(63); 107(70)
4c		1702;	1638;	1492, 1468	264(M^+ , 100); 236(17); 107(52)
4d		1696;	1634;	1487, 1465	346(M^+ , 40); 290(40); 97(100)
4e	1731;	1712;	1642;	1493, 1468	376(M^+ , 67); 289(28); 97(100)
4f		1708;	1633;	1493, 1469, 1433	321(M^+ , 12); 274(65); 100(100)
4g	1735;	1704;	1642;	1494, 1474, 1461	393(M^+ , 7); 274(68); 100(100)
4h		1707;	1632;	1590, 1568, 1488, 1466, 1419	299(M^+ , 36); 252(100); 106(22)
4i	1736;	1714;	1640;	1592, 1568, 1494, 1469, 1421	385(M^+ , 90); 252(100); 106(50)
4j		1710;	1634;	1577, 1556, 1491, 1463, 1418	299(M^+ , 85); 252(60); 92(100)
4k		1702;	1626;	1556, 1490, 1462, 1427	316(M^+ , 75); 283(6); 109(100)
4l	1729;	1709;	1632;	1582, 1489, 1468, 1453	388(M^+ , 66); 315(65); 109(100)
4m		1705;	1636;	1615, 1590, 1551, 1469	316(M^+ , 99); 283(39); 109(100)
4n	1740;	1708;	1642;	1592, 1493, 1470, 1448	388(M^+ , 87); 315(58); 109(100)
4o		1707;	1634;	1599, 1554, 1492, 1465	316(M^+ , 82); 283(5); 109(100)
4p	1741;	1709;	1631;	1558, 1512, 1487, 1467	388(M^+ , 47); 315(20); 109(100)
4q		1702;	1632;	1551, 1491, 1463, 1422	333(M^+ , 32); 297(86); 125(100)
4r	1730;	1713;	1632;	1554, 1492, 1463, 1444	405(M^+ , 7); 369(57); 125(100)
4s		1706;	1633;	1598, 1578, 1493, 1465	333(M^+ , 25); 332(100); 125(87)
4t	1738;	1707;	1642;	1571, 1494, 1468, 1437	405(M^+ , 37); 331(65); 125(100)

Table 5
 ^1H NMR Data of Compounds **2**, **3a** - **k** and **4a** - **t**

No.	^1H NMR (δ/ppm , 300MHz, CDCl_3)
2	7.64 - 6.47(m, 3H, Furyl-H); 7.72(s, 1H, =CH); 4.39 - 4.32(q, 2H, OCH_2CH_3 , J=6.9 Hz); 1.42 - 1.37(t, 3H, OCH_2CH_3 , J = 6.9 Hz).
3a	9.24(bs, 1H, NH); 7.61 - 6.48(m, 3H, Furyl-H); 6.68(s, 1H, =CH); 3.88 - 3.63(t, 2H, NCH_2 , J = 7.4 Hz); 1.81 - 1.69(m, 2H, NCH_2CH_2); 0.99 - 0.94(t, 3H, CH_3 , J = 7.8 Hz).
3b	9.23(bs, 1H, NH); 7.60 - 6.47(m, 3H, Furyl-H); 6.68(s, 1H, =CH); 3.91 - 3.86(t, 2H, NCH_2 , J = 7.3 Hz); 1.72 - 1.65(m, 2H, NCH_2CH_2); 1.42 - 1.34(m, 2H, CH_2CH_3); 0.98 - 0.93(t, 3H, CH_3 , J = 7.3 Hz).
3c	9.30(bs, 1H, NH); 7.60 - 6.47(m, 3H, Furyl-H); 7.26 - 6.93(m, 3H, Thiophen-yl-H); 6.68(s, 1H, =CH); 5.03(m, 2H, NCH_2).
3d	9.25(bs, 1H, NH); 7.60 - 6.47(m, 3H, Furyl-H); 6.68(s, 1H, =CH); 4.04 - 4.01(m, 2H, NCH_2 , J = 5.9 Hz); 3.65 - 3.61(m, 4H, CH_2OCH_2); 2.69(s, 2H, $\text{CH}_2\text{N}(\text{CH}_2)_2$); 2.54(s, 4H, $\text{CH}_2\text{N}(\text{CH}_2)_2$).
3e	9.37(bs, 1H, NH); 8.52 - 7.13(m, 4H, Pyridyl-H); 7.60 - 6.53(m, 3H, Furyl-H); 6.69(s, 1H, =CH); 5.24(s, 2H, NCH_2).
3f	9.38(bs, 1H, NH); 8.74 - 7.21(m, 4H, Pyridyl-H); 7.61 - 6.50(m, 3H, Furyl-H); 6.70(s, 1H, =CH); 5.09(s, 2H, NCH_2).
3g	9.36(bs, 1H, NH); 7.61 - 6.51(m, 3H, Furyl-H); 7.25 - 7.00(m, 4H, Ar-H); 6.70(s, 1H, =CH); 5.17 (s, 2H, NCH_2).
3h	9.33(bs, 1H, NH); 7.60 - 6.49(m, 3H, Furyl-H); 7.26 - 6.91(m, 4H, Ar-H); 6.68(s, 1H, =CH); 5.06 (s, 2H, NCH_2).
3i	9.26(bs, 1H, NH); 7.60 - 6.48(m, 3H, Furyl-H); 7.49 - 6.94(m, 4H, Ar-H); 6.68(s, 1H, =CH); 5.31 (s, 2H, NCH_2).
3j	9.44(bs, 1H, NH); 7.62 - 6.54(m, 3H, Furyl-H); 7.37 - 6.99(m, 4H, Ar-H); 6.71(s, 1H, =CH); 5.21 (s, 2H, NCH_2).
3k	9.29(bs, 1H, NH); 7.60 - 6.49(m, 3H, Furyl-H); 7.43 - 7.21(m, 4H, Ar-H); 6.69(s, 1H, =CH); 5.04 (s, 2H, NCH_2).
4a	7.53 - 6.54(m, 3H, Furyl-H); 6.86(s, 1H, =CH); 3.55 - 3.50(t, 2H, NCH_2 , J = 7.5 Hz); 3.35 - 3.30 (t, 2H, SCH_2 , J = 7.2 Hz); 1.91 - 1.81(m, 2H, NCH_2CH_2); 1.75 - 1.61(m, 2H, SCH_2CH_2); 1.12 - 1.07(t, 3H, $\text{NCH}_2\text{CH}_2\text{CH}_3$, J = 7.2 Hz); 0.95 - 0.91(t, 3H, $\text{SCH}_2\text{CH}_2\text{CH}_3$, J = 7.2 Hz).
4b	7.53 - 6.54(m, 3H, Furyl-H); 6.89(s, 1H, =CH); 4.26 - 4.19(q, 2H, OCH_2 , J = 7.2 Hz); 4.07(s, 2H, SCH_2); 3.58 - 3.53(t, 2H, NCH_2 , J = 7.4 Hz); 1.74 - 1.64(q, 2H, NCH_2CH_2 , J = 7.4 Hz); 1.31-1.26 (t, 3H, OCH_2CH_3 , J = 7.2 Hz); 0.97 - 0.92(t, 3H, $\text{NCH}_2\text{CH}_2\text{CH}_3$, J = 7.4 Hz).
4c	7.54 - 6.54(m, 3H, Furyl-H); 6.87(s, 1H, =CH); 3.60 - 3.55(t, 2H, NCH_2 , J = 7.4 Hz); 2.72(s, 3H, SCH_3); 1.68 - 1.58(m, 2H, NCH_2CH_2); 1.40 - 1.30(m, 2H, CH_2CH_3); 0.96 - 0.91(t, 3H, CH_2CH_3 , J = 7.4 Hz).
4d	7.57 - 6.56(m, 3H, Furyl-H); 7.26 - 6.93(m, 3H, Thiophen-yl-H); 6.94(s, 1H, =CH); 4.93(s, 2H, N-CH_2); 3.42 - 3.73(t, 2H, SCH_2 , J = 6.9 Hz); 1.89 - 1.80(m, 2H, SCH_2CH_2); 1.59 - 1.47(m, 2H, $\text{SCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$); 1.03 - 0.98(t, 3H, CH_2CH_3 , J = 7.4 Hz).
4e	7.53 - 6.54(m, 3H, Furyl-H); 7.23 - 6.91(m, 3H, Thiophen-yl-H); 6.93(s, 1H, =CH); 4.93(s, 2H, NCH_2); 4.25 - 4.18(q, 2H, OCH_2 , J = 7.2 Hz); 4.04(s, 2H, SCH_2); 1.30 - 1.25(t, 3H, OCH_2CH_3 , J = 7.2 Hz).
4f	7.55 - 6.53(m, 3H, Furyl-H); 6.87(s, 1H, =CH); 3.72 - 3.64(m, 6H, NCH_2 and CH_2OCH_2); 2.73(s, 3H, SCH_3); 2.60 - 2.56(m, 2H, NCH_2CH_2); 2.52 - 2.46(m, 4H, $\text{N}(\text{CH}_2)_2$).
4g	7.54 - 6.55(m, 3H, Furyl-H); 6.89(s, 1H, =CH); 4.26 - 4.20(q, 2H, OCH_2CH_3 , J = 6.9 Hz); 4.07(s, 2H, SCH_2); 3.71 - 3.67(m, 6H, NCH_2 and CH_2OCH_2); 2.61 - 2.57(t, 2H, NCH_2CH_2 , J = 6.2 Hz); 2.52 - 2.47(m, 4H, $\text{N}(\text{CH}_2)_2$); 1.32 - 1.27(t, 3H, OCH_2CH_3 , J = 6.9 Hz).
4h	8.54 - 7.15(m, 4H, Pyridyl-H); 7.55 - 6.55(m, 3H, Furyl-H); 6.95(s, 1H, =CH); 4.92(s, 2H, NCH_2); 2.68(s, 3H, SCH_3).
4i	8.53 - 7.17(m, 4H, Pyridyl-H); 7.53 - 6.55(m, 3H, Furyl-H); 6.94(s, 1H, =CH); 4.96 - 4.82(m, 2H, NCH_2); 4.61 - 4.54(q, 1H, SCH, J = 7.2 Hz); 4.28 - 4.10(m, 2H, OCH_2); 1.68 - 1.65(d, 3H, SCH (<i>Me</i>), J = 6.9 Hz); 1.27 - 1.20(m, 3H, OCH_2CH_3).
4j	8.59 - 7.20(m, 4H, Pyridyl-H); 7.55 - 6.55(m, 3H, Furyl-H); 6.93(s, 1H, =CH); 4.77(s, 2H, NCH_2); 2.69(s, 3H, SCH_3).

Table 5 (continued)

No.	^1H NMR (δ /ppm, 300MHz, CDCl_3)
4k	7.55 - 6.55(m, 3H, Furyl-H); 7.31 - 7.03(m, 4H, Ar-H); 6.94(s, 1H, =CH); 4.85(s, 2H, NCH_2); 2.66 (s, 3H, SCH_3).
4l	7.54 - 6.55(m, 3H, Furyl-H); 7.30 - 7.01(m, 4H, Ar-H); 6.95(s, 1H, =CH); 4.86(s, 2H, NCH_2); 4.24 - 4.16(q, 2H, OCH_2CH_3 , $J = 7.2$ Hz); 4.00 (s, 2H, SCH_2); 1.29 - 1.24(t, 3H, OCH_2CH_3 , $J = 7.2$ Hz).
4m	7.54 - 6.54(m, 3H, Furyl-H); 7.26 - 6.94(m, 4H, Ar-H); 6.93(s, 1H, =CH); 4.73(s, 2H, NCH_2); 2.66 (s, 3H, SCH_3).
4n	7.55 - 6.56(m, 3H, Furyl-H); 7.29 - 6.98(m, 4H, Ar-H); 6.96(s, 1H, =CH); 4.77(s, 2H, NCH_2); 4.25 - 4.18(q, 2H, OCH_2CH_3 , $J = 6.9$ Hz); 4.02(s, 2H, SCH_2); 1.29 - 1.25(t, 3H, OCH_2CH_3 , $J = 6.9$ Hz).
4o	7.54 - 6.54(m, 3H, Furyl-H); 7.30 - 6.95(m, 4H, Ar-H); 6.92(s, 1H, =CH); 4.71(s, 2H, NCH_2); 2.67 (s, 3H, SCH_3).
4p	7.54 - 6.55(m, 3H, Furyl-H); 7.31 - 6.96(m, 4H, Ar-H); 6.94(s, 1H, =CH); 4.74(s, 2H, NCH_2); 4.24 - 4.17(q, 2H, OCH_2CH_3 , $J = 7.2$ Hz); 4.03(s, 2H, SCH_2); 1.29 - 1.25(t, 3H, OCH_2CH_3 , $J = 7.1$ Hz).
4q	7.56 - 6.56(m, 3H, Furyl-H); 7.34 - 7.01(m, 4H, Ar-H); 6.97(s, 1H, =CH); 4.91(s, 2H, NCH_2); 2.66 (s, 3H, SCH_3).
4r	7.55 - 6.57(m, 3H, Furyl-H); 7.37 - 7.04(m, 4H, Ar-H); 6.97(s, 1H, =CH); 4.92(s, 2H, NCH_2); 4.24 - 4.16(q, 2H, OCH_2CH_3 , $J = 7.2$ Hz); 4.00(s, 2H, SCH_2); 1.29 - 1.24(t, 3H, OCH_2CH_3 , $J = 7.2$ Hz).
4s	7.55 - 6.55(m, 3H, Furyl-H); 7.31 - 7.10(m, 4H, Ar-H); 6.94(s, 1H, =CH); 4.72(s, 2H, NCH_2); 2.68 (s, 3H, SCH_3).
4t	7.55 - 6.56(m, 3H, Furyl-H); 7.27 - 7.17(m, 4H, Ar-H); 6.95(s, 1H, =CH); 4.75(s, 2H, NCH_2); 4.24 - 4.18(q, 2H, OCH_2CH_3 , $J = 6.8$ Hz); 4.02(s, 2H, SCH_2); 1.29 - 1.25(t, 3H, OCH_2CH_3 , $J = 6.8$ Hz).

Table 6

 ^{13}C NMR Data of Compounds **4e** and **4g**

No.	^{13}C NMR (CDCl_3 , δ / ppm, 300MHz)
4e	166.05(COOEt); 165.37(C=O); 159.04(N=C-S); 148.68, 142.83, 110.95, 110.42(4 Carbons, Furyl); 135.03(CH=C); 132.88, 124.56, 123.79, 115.48(4 Carbons, Thiophen-yl); 125.22(CH=C); 59.84 (OCH ₂); 36.72 (NCH ₂); 30.72 (SCH ₂); 11.73 (OCH ₂ CH ₃).
4g	169.20(COOEt); 169.04(C=O); 162.58(N=C-S); 151.31, 145.28, 113.46, 112.51 (4 Carbons, Furyl); 135.84(CH=C); 117.80(CH=C); 67.10(2 Carbons, CH ₂ OCH ₂); 62.39(OCH ₂); 56.70(CH ₂ N(CH ₂) ₂); 53.88(2 Carbons, CH ₂ N(CH ₂) ₂); 38.263(O=C-NCH ₂); 33.27(SCH ₂); 14.31(OCH ₂ CH ₃)

Table 7

The Fungicidal Activity of Compounds **4a – t**

(50 $\mu\text{g/mL}$, Relative Inhibition %)										
No.	4a	4b	4c	4d	4e	4f	4g	4h	4i	4j
<i>Fusarium oxysporium</i>	53.8	23.1	42.3	53.8	13.0	13.0	13.0	13.0	33.3	21.7
<i>Botryosphaeria berengeriana</i>	33.3	33.3	26.7	33.3	0	40.0	6.7	0	41.6	0
<i>Rhizoctonia solani</i>	25.0	50.0	55.3	62.5	20.0	50.0	25.0	12.5	28.6	25.0
No.	4k	4l	4m	4n	4o	4p	4q	4r	4s	4t
<i>Fusarium oxysporium</i>	22.2	44.4	61.1	55.6	61.1	11.7	5.6	88.9	61.1	55.6
<i>Botryosphaeria berengeriana</i>	62.5	62.5	50.0	68.7	50.0	0	50.0	62.5	50.0	75.0
<i>Rhizoctonia solani</i>	48.6	57.1	42.8	37.1	42.8	25.0	60.0	65.7	42.8	37.1

cm^{-1} due to C=C group, at 1263 cm^{-1} due to C=S group. The ir spectral data of compounds **3a - k** showed absorption bands in the $3308 - 3120\text{ cm}^{-1}$ range due to N-H group, in the $1740 - 1715\text{ cm}^{-1}$ range due to C=O group, in the $1655 - 1647\text{ cm}^{-1}$ range due to C=C group on the side chain of imidazolinone, and in the $1160 - 1115\text{ cm}^{-1}$ range due to the C=S group. The ir spectral data of compounds **4a - t** was also sound. For example, the ir spectral data of **4n** showed a strong absorption bands for the C=O group on the side chain COOEt at 1740 cm^{-1} , a strong absorption bands for C=O group in the imidazolinone framework at 1708 cm^{-1} . The resonance absorption bands of the Aryl and furyl framework are observed at 1493 , 1470 , and 1448 cm^{-1} . In addition to the two relatively strong absorption bands at 1642 and at 1592 cm^{-1} , which can be assigned to the C=C

group on the side chain of imidazolinone and C=N group in the imidazolinone framework, respectively.

The ^1H nmr spectra of compounds **3a - k** exhibited a broad singlet signal in the δ 9.23 - 9.44 range accounting for the proton of N-H, a sharp singlet signal in the δ 6.68 - 6.69 range accounting for the alkenyl hydrogen on the side chain of imidazolinone, multiple signals in the δ 7.62 - 6.47 range accounting for 3 hydrogens of furyl group, multiple signals in the δ 7.49 - 6.91 range accounting for 4 hydrogens of aryl group, in the δ 8.52 - 7.13 range with multiple signals for the 4 hydrogens of pyridyl group, and multiple signals in the δ 7.26 - 6.93 range accounting for the 3 hydrogens of thiophenyl group. The ^1H nmr spectra of compounds **4a - t** are explained with compound **4n** as an example, which exhibited multiple signals in the δ 7.55

Table 8
The Herbicidal Activity of Compounds **4a - t**
(Relative Inhibition %) [d]

No.	Cole		Barnyard grass	
	100 $\mu\text{g}/\text{mL}$ (Root/Stalk)	10 $\mu\text{g}/\text{mL}$ (Root/Stalk)	100 $\mu\text{g}/\text{mL}$ (Root/Stalk)	10 $\mu\text{g}/\text{mL}$ (Root/Stalk)
4a	18.2 / 50.0	17.2 / 33.3	-6.0 / 47.2	-14.0 / 44.4
4b	17.2 / 37.0	15.2 / 33.3	6.0 / 63.9	6.0 / 44.4
4c	76.1 / 49.1	32.7 / 24.6	86.5 / 59.5	45.9 / 37.8
4d	36.4 / 40.7	30.3 / 31.5	4.0 / 44.4	4.0 / 41.7
4e	69.8 / 6.7	25.0 / 0	70.0 / 9.1	37.5 / 13.6
4f	55.2 / 26.7	25.0 / 8.9	55.0 / 22.7	15.0 / 18.2
4g	79.3 / 28.9	44.8 / 24.4	57.5 / 13.6	50.0 / 13.6
4h	49.1 / 4.4	34.5 / 0	72.5 / 9.1	52.5 / 9.1
4i	49.5 / 22.8	24.8 / 10.5	67.6 / 37.8	35.1 / 32.4
4j	62.9 / 31.1	44.8 / 26.7	65.0 / 13.6	65.0 / 10.9
4k	52.2 / -7.7	27.8 / -7.7	75.5 / 5.3	71.4 / 5.3
4l	26.1 / 15.4	24.3 / 5.1	40.8 / 36.8	40.8 / -10.5
4m	24.3 / 0	19.1 / 0	69.4 / -10.5	36.7 / -10.5
4n	35.6 / 2.6	9.6 / 0	77.6 / 5.3	48.9 / -5.3
4o	28.7 / 10.3	18.3 / -5.1	71.4 / 26.3	55.1 / -5.3
4p	94.8 / 89.7	35.4 / 39.7	96.0 / 77.1	68.0 / 25.0
4q	56.5 / 12.8	26.1 / 10.3	75.5 / 5.3	16.3 / -15.8
4r	77.4 / 41.0	33.9 / 25.6	89.9 / 0	73.5 / 0
4s	29.6 / 2.6	17.4 / 0	77.6 / -15.8	48.9 / -31.6
4t	23.5 / -17.9	17.4 / -20.5	46.9 / 21.0	42.8 / 0
2,4-D	99.2 / 98.0	97.9 / 96.7	99.9 / 65.8	98.4 / 66.6

[d] positive: growth inhibition; minus: promotion growth; 0 % = no effect, 100 % = complete killing. 2,4-D: (2,4-dichloro-phenoxy)-acetic acid.

- 6.56 range accounting for the 3 hydrogens of furyl group, multiple signals in the δ 7.29 - 6.94 range accounting for the 4 hydrogens of aryl group. The chemical shift of the alkenyl hydrogen on the side chain of imidazolinone was observed at δ 6.96 with a single signal, δ 4.77 and δ 4.02 with a single signal accounting for the 2 hydrogens of NCH_2 and SCH_2 , respectively. Four signals with $J = 6.9$ Hz in the range δ 4.25 - 4.18 for the 2 hydrogens of OCH_2CH_3 group, three signals with $J = 6.9$ Hz in the range δ 1.29 - 1.25 for the 3 hydrogens of OCH_2CH_3 group (see Table 5).

The ^{13}C nmr spectra for compounds **4e** and **4g** were consistent with the assigned structures (see Table 6).

The EI-mass spectra of most of compounds **2**, **3a - k** and **4a - t** except **3j** and **3k** exhibited strong molecule ion peaks (see Table 3 and Table 4). Compounds **3j** and **3k** showed fragment ion peaks corresponding to $[\text{M}+1]^+$ at m/z 320 and $[\text{M}-1]^+$ at m/z 318, respectively, instead of the molecular ion peak of M^+ at m/z 319. The major fragmentation pathways are explained with that of compound **4n** as an example, which showed a strong molecular ion peak M^+ with m/z 388 and 87 % relative abundance. The fragmentation pathways of **4n** are rationalized in Scheme 2.

The biological activities of all compounds **4a - t** were investigated and the results of bioassay showed that they

exhibited herbicidal and fungicidal activities (see Table 7 and Table 8). Especially, in 50 $\mu\text{g}/\text{mL}$, **4r** showed 88.9 % inhibition of *Fusarium oxysporium*. In 100 $\mu\text{g}/\text{mL}$, **4p** showed 94.8 % inhibition of Cole root, 89.7 % inhibition of Cole stalk, and 96.0 % inhibition of Barnyard grass root. Compounds **4c** and **4r** showed 86.5 % and 89.9 % inhibition of Barnyard grass root in 100 $\mu\text{g}/\text{mL}$, respectively. To some extent, compounds **4s** and **4t** showed promotion growth of Barnyard grass stalk and Cole stalk, respectively.

EXPERIMENTAL

Chemistry.

Melting points were determined on an X4 melting-point apparatus, and are not corrected; Elemental analyses were taken on a PE-2400-CHN elemental analysis instrument. The ir spectra were recorded on a Perkin-Elmer-1600 FT Infrared spectrometer in KBr pellets (ν in cm^{-1}). The ^1H and ^{13}C nmr were measured in CDCl_3 on a Varian XL-300 spectrometer with TMS as an internal standard (δ in ppm). The Mass spectra were recorded on a Finnigan TRACE GC-MS spectrometer at an ionization potential 70 eV. Thin layer chromatography was employed to follow the progress of all synthetic reactions.

The vinyliminophosphorane **1** was prepared according to the literature report [18].

General Procedure for the Preparation of **2**.

A solution of 2.21 g, 5 mmoles vinyliminophosphorane **1** in 20 mL dry dichloromethane and 3.5 g, 50 mmoles carbon disulfide was refluxed for 29 hours under stirring and the protection of a nitrogen atmosphere, and then allowed to cool to room temperature. The solvent and excess carbon disulfide was removed *in vacuo*. The residue was dissolved completely in 15 mL dichloromethane, and a 30 mL mixture of ether and petroleum ether (1:2, volume ratio) was added to precipitate the triphenylphosphine sulfide. The solution was filtered, and the filtrate was condensed *in vacuo* keeping the temperature $< 40^\circ\text{C}$, and the residual was recrystallized from a 20 mL mixture of ether and petroleum ether (1:3, volume ratio) to yield 3-furan-2-yl-2-isothiocyanato acrylic acid ethyl ester **2**.

General Procedure for the Synthesis of 2-Thio-4-imidazolinones **3**.

To a solution of **2** prepared above in 20 mL dry dichloromethane was added RNH_2 (if $\text{R} = \text{Pr}$ or Bu , 5 mmoles; if $\text{R} = \text{Benzyl}$ -typed alkyl, 3 mmoles). The mixture was stirred for 0.5 - 3 hours at room temperature and filtered, the solvent and excess RNH_2 in the filtrate was evaporated *in vacuo*. The residual was recrystallized from a 20 mL mixture of dry dichloromethane and petroleum ether (1:3, volume ratio) to obtain **3**.

General Procedure for the Synthesis of 2-Alkylthio-4-imidazolin-4-ones **4**.

A mixture of 3 mmoles **3** in 10 mL dry acetonitrile, 3.5 - 5 mmoles $\text{R}'\text{X}$, and 3.33 g, 24 mmoles $\text{K}_2\text{CO}_3(\text{s})$ was stirred for 1 - 5 hours at room temperature or $40 - 60^\circ\text{C}$, and was allowed to stand in order to precipitate the solid potassium carbonate completely.

The mixture was filtered, the filtrate was condensed, and the residual was recrystallized from a 20 mL mixture of dry dichloromethane and petroleum ether (1:4, volume ratio) to yield **4**.

Biological Testing.

The newly synthesized compounds **4a-t** were tested for fungicidal activities against specified microorganisms such as *Fusarium oxysporium*, *Botryosphaeria berengeriana* and *Rhizoctonia solani*, using 400 µg/mL (w/v) solutions in sterile acetone, respectively. The concentration of each tested compound was made 50 µg/mL with sterile acetone, emulsifier and distilled water. A 50 µg/mL solution of the tested compound was poured aseptically in a well of 5 mm diameter made by a borer in a seeded agar medium, respectively. The distilled water was used as a comparison compound. After pipetting the same volume in wells of all tested microorganisms, respectively, pathogen test plates were incubated at 37 °C for 24 hours, fungal test plates and the comparison plate were incubated at 25 °C for 48 hours. The activities were expressed as inhibition rate (inhibition zones in diameter, mm, as clear areas) in comparison with distilled water.

Herbicidal testing of the newly synthesized compounds **4a-t** was carried out in a plant growth room, temperature 23±1 °C, RH 60±5 %, light intensity 10 klux, photoperiod 8 hours. Twenty seeds of each one of weed species including Barnyard grass (*Echinochloa crusgalli*) and Cole (*Brassica campestris* Var. Oleifera) were chosen for testing. Seedlings were grown in the test plate of 9 cm diameter containing two pieces of filter paper and 9 mL solution of the tested compound (10 and 100 µg/mL, respectively). Distilled water and (2,4-dichlorophenoxy)-acetic acid (2,4-D) were used as comparison compounds. The herbicidal activity was assessed as the inhibition rate in comparison with the distilled water and (2,4-dichlorophenoxy)acetic acid 8 days after treatment. The herbicidal rating score based on visual observation, range from 0 % to 100 %; 0 % = no effect, 100 % = complete killing.

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