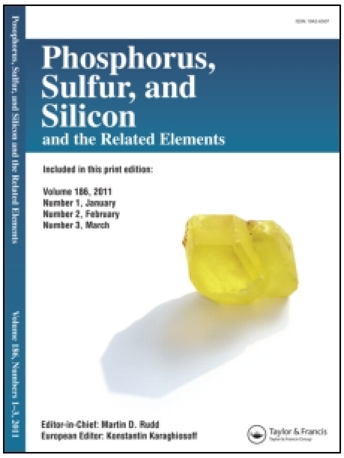

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NOVEL SULFUR CONTAINING AGRO CHEMICALS: SYNTHESIS OF MERCAPTOTRIAZOLES, TRIAZOLO-(3,4-b)-THIADIAZOLE, TRIAZOLO-(3,4-b)-THIADIAZINE AND TRIAZOLO-(3,4-b)-THIADIAZEPINE RING SYSTEMS AS POSSIBLE FUNGITOXIC AGENTS

M. A. Hanna[a]; M. N. Khodeir[a]; M. A. Mashaly[a]; H. M. El-shafei[a]
[a] Chemistry Department, Damiatta Faculty of Science, Mansoura University, Mansoura, Egypt

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NOVEL SULFUR CONTAINING AGRO CHEMICALS: SYNTHESIS OF MERCAPTOTRIAZOLES, TRIAZOLO-(3,4-b)-THIADIAZOLE, TRIAZOLO-(3,4-b)-THIADIAZINE AND TRIAZOLO-(3,4-b)-THIADIAZEPINE RING SYSTEMS AS POSSIBLE FUNGITOXIC AGENTS

M. A. HANNA,† M. N. KHODEIR, M. A. MASHALY and
H. M. EL-SHAFEI

Chemistry Department, Damiatta Faculty of Science, Mansoura University,
PO 48, Mansoura Univ., 35516 Mansoura, Egypt

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A series compounds **II–XII** have been synthesized from the stereo-isomeric 4-{4-(Z)-[*p*-(benzenesulfonyloxy)phenylmethylene]-5-oxo-1-phenyl-2-imidazolin-1-yl)-benzoic acid hydrazide derivative (**I**) in order to investigate the fungitoxic activity of the compounds against Rice blast pathogen "Pyricularia oryzae" and Brown leaf spot pathogen "Helminthosporium oryzae" and the possibility of their use as new sulfur-containing agro chemicals. Fungitoxicity of most of the synthesized products compared well with a standard commercial fungicide. The assigned structures for these potential fungitoxic agents were established by elemental analyses, spectral data and whenever possible by alternative synthetic routes.

Key words: Synthesis; fungitoxicity; imidazolyl-mercaptotriazoles; triazolo-(3,4-b)-thiadiazole; Triazolo-(3,4-b)-thiadiazine and triazolo-(3,4-b)-thiadiazepine ring systems.

In view of the broad spectrum of biological activities associated with thiosemicarbazides and mercaptotriazoles, numerous compounds[1-3] containing such moieties have been studied. Some s-triazolo-[3,4-b]-1,3,4-thiadiazoles were reported[4,5] to exhibit various biological activities. In continuation of our program[6,7] pertaining to the synthesis of novel sulfonate ester-containing heterocycles with predicted biological activities, we report here on the stereospecific synthesis of the previously unreported 4-{4-(Z)-[*p*-(benzenesulfonyloxy)phenylmethylene]-5-oxo-1-phenyl-2-imidazolin-1-yl}benzoic acid hydrazide derivative (I) and its use, *via* latent active functions, as a key intermediate for the synthesis of various sulfur-containing isolated or fused ring systems of extended and/or improved antifungal activity.

The synthesis of the title compounds followed the reaction sequences shown in Schemes 1 and 2.

The starting compound (I) was obtained by treating ethyl 4-{4-(Z)-[*p*-(benzenesulfonyloxy)phenylmethylene]-5-oxo-1-phenyl-2-imidazolin-1-yl}benzoate[8] with hydrazine hydrate (99%) in absolute ethanol.

Besides the normal absorption bands, assignable to tertiary amidic linkage, C=N— and sulfonate ester moieties, the IR spectrum of the hydrazide exhibited several absorptions at 3540, 3460, 3410, and 1665 cm^{-1} that might be attributed to NH_2, NH and the carbonyl group of hydrazide moiety, respectively.

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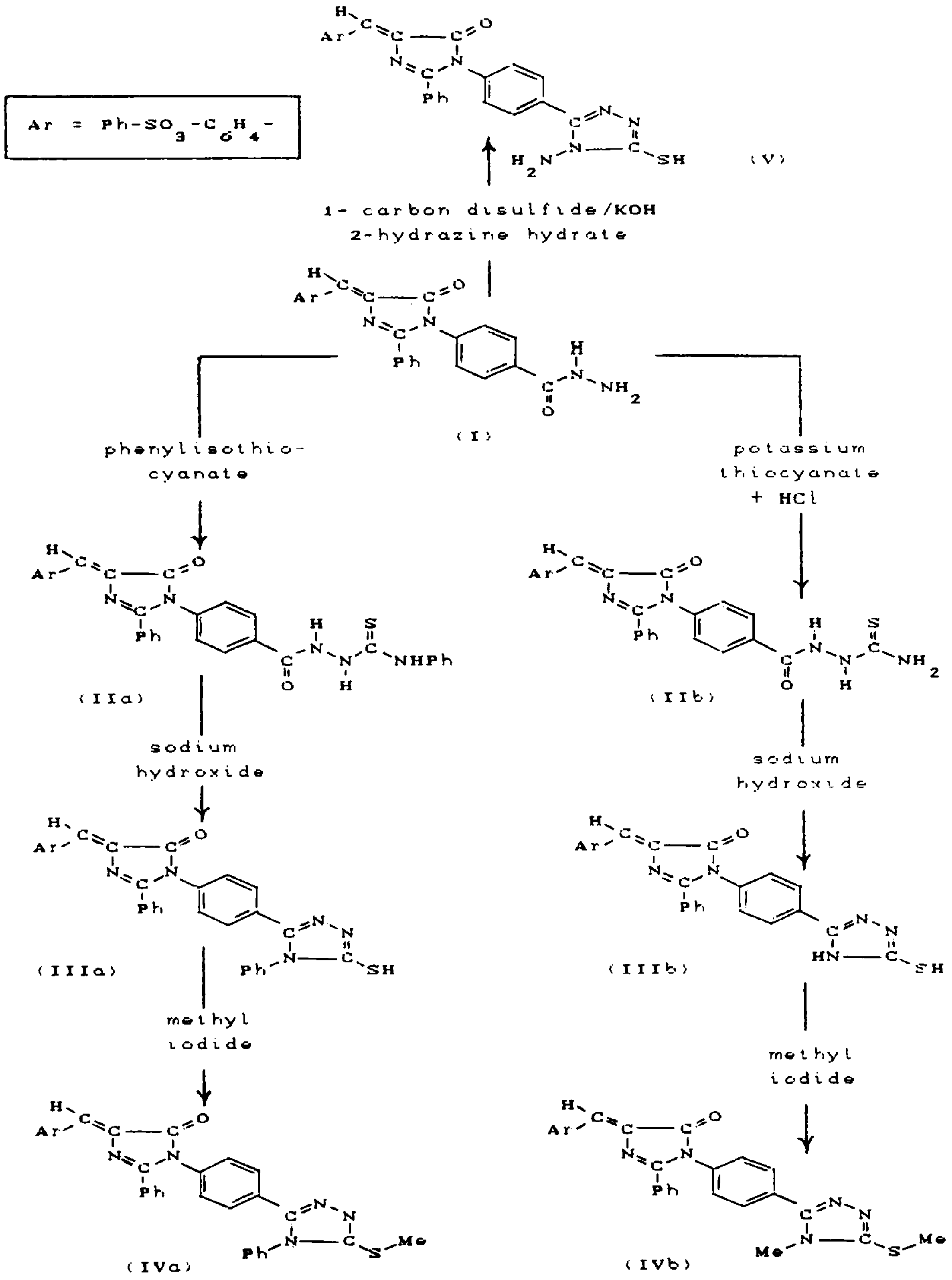
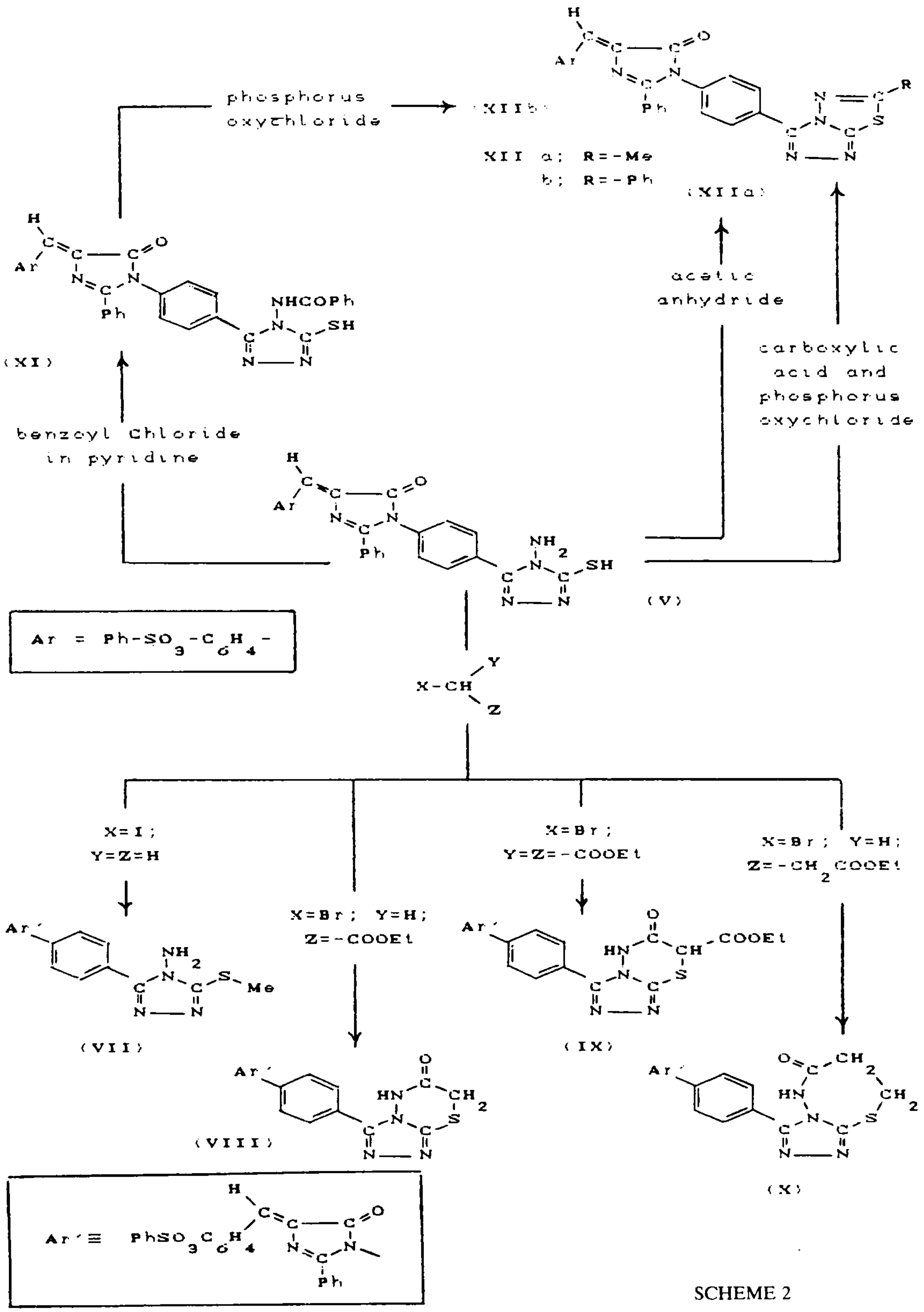
†To whom all correspondence should be addressed.


Ar = Ph-SO$_3$-C$_6$H$_4$-
(V)
1- carbon disulfide/KOH
2-hydrazine hydrate
(I)
phenylisothio-cyanate
potassium thiocyanate + HCl
(IIa)
(IIb)
sodium hydroxide
sodium hydroxide
(IIIa)
(IIIb)
methyl iodide
methyl iodide
(IVa)
(IVb)

SCHEME 1


phosphorus oxychloride
(XIIb)
XII a; R = -Me
b; R = -Ph
(XIIa)
acetic anhydride
carboxylic acid and phosphorus oxychloride
(XI)
benzoyl chloride in pyridine
(V)
Ar = Ph-SO3-C6H4-
X-CH(Y)(Z)
X = I; Y = Z = H
X = Br; Y = H; Z = -COOEt
X = Br; Y = Z = -COOEt
X = Br; Y = H; Z = -CH2COOEt
(VII)
(VIII)
(IX)
(X)
Ar′ ≡ PhSO3C6H4

SCHEME 2

The 1-[4-{4-(Z)-[*p*-(benzenesulfonyloxy)phenylmethylene]-5-oxo-1-phenyl-2-imidazolin-1-yl}benzoyl]-4-phenylthiosemicarbazide (**IIa**) was obtained in good yield by refluxing the hydrazide derivative (**I**) with phenylisothiocyanate in absolute ethanol.

The IR spectrum of this compound exhibited stretching vibrations at 3350–3150, 1700, 1680, 1625, 1365, 1160, and 1110 cm^{-1} corresponding to NH functions, tertiary-amidic carbonyl, —CONH—, C═N—, asym. and sym. stretching vibrations of —SO_3— and —C═S moieties, respectively.

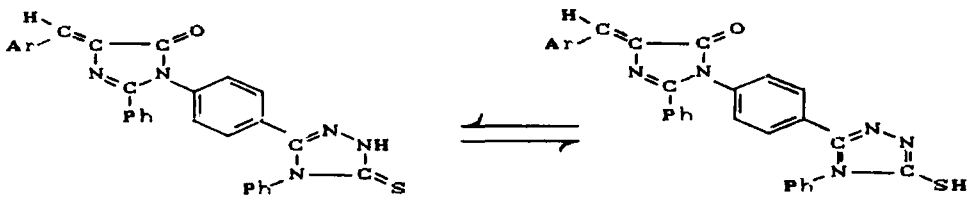
Alkaline cyclization of the above thiosemicarbazide, **IIa**, yielded 3-[4-{4-(Z)-[*p*-(benzenesulfonyloxy)phenylmethylene]-5-oxo-1-phenyl-2-imidazolin-1-yl}phenyl]-4-phenyl-5-mercapto-4H-1,2,4-triazole derivative (**IIIa**). The 3-(imidazolin-1-yl-phenyl)-5-mercapto-4H-1,2,4-triazole (**IIIb**) was prepared by the cyclization of 1-(imidazolin-1-yl-phenyl) thiosemicarbazide (**IIb**) which was obtained by the effect of potassium thiocyanate and concentrated hydrochloric acid on (**I**). The IR spectrum of **IIIa** was comparable with those reported earlier.[9] The presence of a strong absorption band at 1120 cm^{-1} showed its possible existence in the thione form (A), but a weak band at 2570 cm^{-1} also indicated the presence of the thiol form (B) in a tautomeric equilibrium.[10] Besides phenyl pattern in the ^{1}H-NMR spectrum of this product in (DMSO-d_6), another broad, D_2O-exchangable, signal appeared at 1.86 ppm that might be ascribed to SH proton of the thiol tautomer B.

Further support for the possible existence of the tautomers **IIIa** and **IIIb** was obtained via their methylation. The S-methylation was confirmed by the presence of a singlet at δ 2.30 ppm, in the ^{1}H-NMR spectrum of the methylation product (**IVa**); for the 3-substituted 4H-1,2,4-triazole derivative (**IVb**) two singlets at δ 2.25 and 3.85 ppm were observed confirming the methylation of both of S- and N-atoms, respectively, Scheme 1.

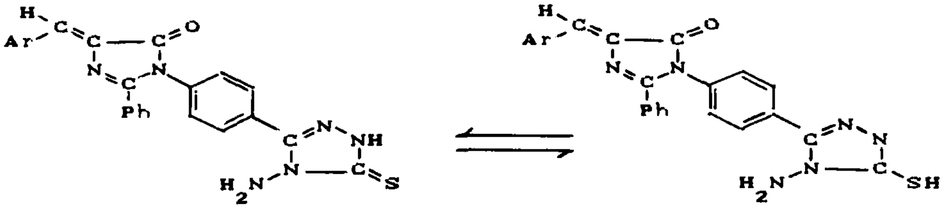
The potential use of hydrazides of type I as a key intermediate for the synthesis of different *s*-triazoles and/or their fused ring systems was extended to prepare the 4-amino-3-[4- {4-(Z)-[*p*-(benzenesulfonyloxy)phenylmethylene]-5-oxo-1-phenyl-2-imidazolin-1-yl}phenyl]-5-mercapto-4H-1,2,4-triazole derivative (**V**).

Treatment of **I** with potassium hydroxide and carbon disulfide in absolute ethanol[11] afforded the required product via cyclization of the non isolable potassium dithiocarbazate intermediate. Spectral data for this compound revealed that similar to the triazoles **IIIa** and **IIIb**, the product **V** exists in a tautomeric equilibrium of the thione form (**V-A**) as well as the thiol structure (**V-B**), (cf. experimental part).

The presence of the basic N-amino function in (**V**) was confirmed via its condensation with aromatic aldehydes in the presence of glacial acetic acid and a catalytic amount of freshly fused sodium acetate. The newly inserted arylidene-

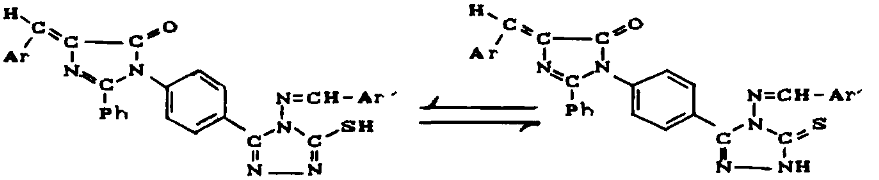


(III-A) (III-B)



(V-A) (V-B)

amino function adds a further possibility for the presence of two different geometrical, (Z,Z) & (Z,E), isomers.



VIa; Ar= $PhSO_3-C_6H_4-$; Ar′= C_6H_5

b; Ar= $PhSO_3-C_6H_4-$; Ar′= C_6H_4-Cl-p

Attempts to separate these two different isomers by fractional crystallization were unsuccessful. The IR spectra of the produced 4-arylideneamino-3-[4-{4-(Z)-[*p*-(benzenesulfonyloxy)phenylmethylene]-5-oxo-1-phenyl-2-imidazolin-1-yl} phenyl]-5-mercapto-4H-1,2,4-triazole derivatives (**VIa,b**) revealed the absence of absorption bands above 3150 cm^{-1} (for the basic N-amino group) and the appearance of characteristic absorption peaks near 3150, 2565, 1625, 1620 and 1110 cm^{-1} that might be ascribed to stretching vibrations of NH, SH, cyclic and acyclic C=N grouping, respectively. The presence of proton signals at 9.54 ppm ($C\underline{H}$=N) and 1.71 ppm ($S\underline{H}$, exchangable with D_2O) in ^1H-NMR spectrum of compound (**VIa**) not only substantiates the chemical structure of these new products but also confirms the possibility of their existence in a tautomeric equilibrium of thiol and thione structures.

While reaction of (V) with iodomethane in acetone and in the presence of anhydrous potassium carbonate gave the corresponding methyl thioether analogue (VII), the reaction of (V) with halo-esters namely, ethyl bromoacetate, ethyl bromomalonate, and ethyl β-bromopropionate afforded the corresponding 1,2,4-triazolo-(3,4-b)-1,3,4-thiadiazine (VIII), 2-ethoxycarbonyl-1,2,4-triazolo-(3,4-b)-1,3,4-thiadiazine (IX) and 1,2,4-triazolo-(3,4-b)-1,3,4-thiadiazepine (X) fused ring systems, respectively. The structure of these fused ring systems was established based on their elemental analyses and their spectral data. The appearance of a common absorption band near 1665 cm^{-1}, for amide I band of cyclic amide moiety, in IR spectra of structures **VIII**, **IX** and **X** (cf. experimental part) apparently substantiates the formation of these fused ring systems.

Further application for the use of compound (V) in the synthesis of additional fused ring systems, as for **XIIa,b**, was achieved via its direct treatment with carboxylic acids in presence of phosphorus oxychloride or acetic anhydride as was shown in the case of compound **XIIa**. A second route for the preparation of compound **XIIb** was affected *via* prior preparation of the N-benzoyl derivative (XI), by action of benzoyl chloride in pyridine and subsequent cyclization in the presence of phosphorus oxychloride.

The produced 4-[4-{4-(Z)-[*p*-(benzenesulfonyloxy)phenylmethylene]-5-oxo-1-phenyl-2-imidazolin-1-yl}phenyl] 2-substituted 1,2,4-triazolo(3,4-b)-1,3,4-thiadiazole derivatives (**XIIa,b**) did not show IR-absorption bands corresponding to stretching vibrations of thioxo, mercapto and/or secondary-amidic carbonyl moieties.

EXPERIMENTAL

The homogenicity and purity of the prepared compounds were checked by TLC. Melting points of the analytical samples were determined using Fisher-Johns apparatus and are not corrected. IR spectra were recorded on a Specord M-80 spectrophotometer using (KBr) pellets. ^{1}H-NMR spectra were determined on a Varian EM 360 spectrometer 80 MHz and on a Varian EM 390, 90 MHz spectrometer relative to TMS as an internal standard. Nomenclature of the hitherto prepared compounds is given in accordance with IUPAC rules for nomenclature of organic compounds.

4-{4-(Z)-[p-(Benzenesulfonyloxy)phenylmethylene]-5-oxo-1-phenyl-2-imidazolin-1-yl}benzoic acid hydrazide derivative (**I**). A solution of ethyl 4-{4-(Z)-[*p*-(benzenesulfonyloxy)phenylmethylene]-5-oxo-1-phenyl-2-imidazolin-1-yl}benzoate (0.001 mol) and hydrazine hydrate (99%; 0.0012 mol) in absolute ethanol (10 ml) was refluxed for 10 h. After cooling the precipitate was filtered off, washed with water, dried and recrystallized from ethanol as colorless crystals, m.p. 150–152°C. IR spectrum (cm^{-1}): 3540. 3460 (NH$_2$), 3410 (NH), 1690 (cyclic tertiary-amidic linkage), 1665 (CO of hydrazide moiety), 1625 (—C=N—), 1365 & 1160 (SO$_3$ function).

1-[4-{4-(Z)-[p-(Benzenesulfonyloxy)phenylmethylene]-5-oxo-1-phenyl-2-imidazolin-1-yl}benzoyl]-4-phenylthiosemicarbazide (**IIa**). To a suspension of (**I**) (5.4 g, 0.01 mol) in absolute ethanol (20 ml) was added phenyl isothiocyanate (0.012 mol) and the mixture was shaken for 10 min and refluxed for 8 h. Cooling to room temperature afforded a yellowish white solid which was filtered off, washed with ethanol and recrystallized from the same solvent as yellowish-white needles of m.p. 185–187°C. IR spectrum (cm^{-1}): broad peak at 3350–3150 (NH functions), 1700 (cyclic tertiary-amidic linkage), 1690 (CONH), 1625 (C=N), 1365 & 1160 (SO$_3$ group) and 1110 (—C=S).

1-[4-{4-(Z)-[p-(Benzenesulfonyloxy)phenylmethylene]-5-oxo-1-phenyl-2-imidazolin-1-yl}benzoyl] thiosemicarbazide (**IIb**). A mixture of (**I**), (5.4 g, 0.01 mol), potassium thiocyanate (1.94 g, 0.02 mol), conc. hydrochloric acid (12 ml) and water (150 ml) was refluxed for 7 h and cooled. The solid that separated out was filtered off, washed with water and recrystallized from ethanol to give **IIb** as white crystals of m.p. 180–182°C. IR spectrum (cm^{-1}): 3410–3200 (amino and NH function), 1700 (tertiary-amidic CO), 1680 (—CONH—), 1625 (C=N), 1365 & 1160 (asym. & sym. stretching of sulfonate ester moiety) and 1100 (—C=S).

3-[4-{4-(Z)-[p-(Benzenesulfonyloxy)phenylmethylene]-5-oxo-1-phenyl-2-imidazolin-1-yl}phenyl]-5-mercapto-4H-1,2,4-triazole derivatives (**IIIa,b**). A suspension of **IIa** or **IIb** (0.01 mol) in sodium hydroxide solution (5%, 15 ml) was refluxed for 8 h and cooled. The resulting solution was treated with charcoal, filtered and the filtrate was acidified with dil HCl to pH 5–6. The precipitated solid was filtered and recrystallized from aqueous ethanol as yellowish coloured crystals. IR spectrum of **IIIa** (cm^{-1}): 3140 (NH), 2570 (SH), 1695 (tertiary-amidic CO), 1625 (—C=N—), 1365, 1160 (sulfonate ester moiety) and a strong band at 1120 cm^{-1} (—C=S). ^{1}H-NMR spectrum (δ/ppm) of the same product in (DMSO-d$_6$): 7.80–6.75 (m, 24H, 23 Ar-H + ylidene proton) and at 1.86 (br., exhangable 1H, of thiol moiety).

3-[4- {4-(Z)-[p-(Benzenesulfonyloxy)phenylmethylene]-5-oxo-1-phenyl-2-imidazolin-1-yl}phenyl]-5-methylthio-4-substituted 4H-1,2,4-triazole derivatives (**IVa,b**). Iodomethane (0.001 mol) was added to a mixture of methanolic solution of **IIIa** or **IIIb** (0.001 mol) and freshly fused sodium acetate (0.1 g). The whole mixture was refluxed for 7 h then cooled, poured onto crushed ice and allowed to stand overnight in a refrigerator. The separated solid was filtered off, washed with methanol and recrystallized from the same solvent to give the required products (cf. Table I). ^{1}H-NMR spectrum (δ/ppm) of (**IVa**)

TABLE I

Characterization data of the synthesized sulfonate ester-containing agro chemicals (**I–XII**)

Sl. no.	M.p. °C Yield (%)	Formula (M. Wt.)	Fungitoxic activity % Inhibition at 500 ppm		Analyses Calcd./Found		
			P. oryzae	*H. oryzae*	%C	%H	%S
I	150–152	$C_{29}H_{22}N_4O_5S$	68	73	64.67	04.12	05.59
	(68)	(538.56)			64.50	04.18	05.73
IIa	185–187	$C_{36}H_{27}N_5O_5S_2$	73	56	64.17	04.04	09.52
	(75)	(673.74)			63.92	04.16	09.44
IIb	180–182	$C_{30}H_{23}N_5O_5S_2$	60	71	60.29	03.88	10.73
	(66)	(597.64)			60.51	04.02	10.98
IIIa	128–130	$C_{36}H_{25}N_5O_4S_2$	66	73	65.94	03.84	09.78
	(71)	(655.72)			66.05	03.90	09.65
IIIb	>300	$C_{30}H_{21}N_5O_4S_2$	54	50	62.16	03.65	11.06
	(63)	(579.63)			61.99	03.72	10.95
IVa	218–220	$C_{37}H_{27}N_5O_4S_2$	63	61	66.35	04.06	09.57
	(55)	(669.75)			66.40	04.15	09.53
IVb	>300	$C_{32}H_{25}N_5O_4S_2$	72	58	63.24	04.15	10.55
	(69)	(607.68)			63.46	04.12	10.72
V	266–267	$C_{30}H_{22}N_6O_4S_2$	44	39	60.59	03.73	10.78
	(59)	(594.65)			60.81	03.79	10.58
VIa	72–74	$C_{37}H_{26}N_6O_4S_2$	49	32	65.09	03.84	09.39
	(62)	(682.75)			64.82	03.79	09.50
VIb	204–206	$C_{37}H_{25}ClN_6O_4S_2$	43	51	61.96	03.51	08.94
	(69)	(717.19)			62.08	03.50	09.01
VII	151–153	$C_{31}H_{24}N_6O_4S_2$	62	68	61.17	03.97	10.53
	(54)	(608.67)			60.95	03.99	10.59
VIII	118–120	$C_{32}H_{22}N_6O_5S_2$	73	65	60.55	03.49	10.10
	(45)	(634.67)			60.66	03.58	09.94
IX	131–133	$C_{35}H_{26}N_6O_7S_2$	79	85	59.48	03.71	09.07
	(68)	(706.73)			59.61	03.74	09.03
X	106–108	$C_{33}H_{24}N_6O_5S_2$	70	77	61.10	03.73	09.88
	(51)	(648.69)			61.22	03.72	10.02
XI	244–245	$C_{37}H_{26}N_6O_5S_2$	62	51	63.59	03.75	09.18
	(70)	(698.75)			63.66	03.69	09.26
XIIa	254–255	$C_{32}H_{22}N_6O_4S_2$	59	57	62.12	03.59	10.36
	(64)	(618.67)			62.08	03.67	10.47
XIIb	135–137	$C_{37}H_{24}N_6O_4S_2$	73	68	65.28	03.55	09.42
	(62)	(680.73)			65.07	03.61	09.52

in ($CDCl_3$ + DMSO-d_6): 7.75–6.80 (m, 24H, 23H Ar-H + ylidene proton) and 2.30 (s, 3H, —S—C$\underline{H}_3$). For compound (**IVb**), the two N- and S-methyl protons appeared at 3.85 and 2.25 ppm, respectively.

4-Amino-3-[4- {4-(Z)-[p-(benzenesulfonyloxy)phenylmethylene]-5-oxo-1-phenyl-2-imidazolin-1-yl}-phenyl]-5-mercapto-4H-1,2,4-triazole derivative (**V**). To a solution of (**I**) (5.4 g, 0.01 mol) in ethanolic potassium hydroxide (0.9 g in 30 ml), carbon disulphide (0.015 mol) was added at room temperature with continuous stirring and the mixture was kept stirred for a further 18 h at the same temperature. The precipitated solid was collected by filtration, washed with ether dried and suspended in hydrazine hydrate (99%, 2 ml) and refluxed for 5 h. Cold water (25 ml) was added and the whole mixture was neutralized with dilute hydrochloric acid. The so formed crude product was filtered, washed with water, dried and recrystallized from ethanol to give the pure product. Characterization data for this compound is given in Table I. IR spectrum (cm^{-1}) reveals absorption bands at 3480, 3400 (amino group), 3160 (NH), 2565 (SH), 1700 (tertiary-amidic linkage), 1625 (C═N), 1365 and 1160 (sulfonate ester moiety) and 1100 (C═S). ^{1}H-NMR spectrum (δ/ppm) of (**V**) in (DMSO-d_6): 7.75–6.80 ppm (m, 19H, 18 for Ar-H and 1H of ylidene moiety), 5.15 ppm (br., 2H, exchanged with D_2O, amino group) and at 1.82 ppm (br., 1H, exchanged with D_2O, thiol proton).

4-Arylideneamino-3-[4- {4-(Z)-[p-(benzenesulfonyloxy)phenylmethylene]-5-oxo-1-phenyl-2-imidazolin-1-yl} phenyl]-5-mercapto-4H-1,2,4-triazole derivatives (**VIa,b**). A mixture of (**V**) (5.9 g, 0.01 mol), aromatic aldehyde (0.012 mol) and a catalytic amount of freshly fused sodium acetate (0.5 g) in glacial acetic acid (10 ml) was refluxed for 5 h and cooled. The solid that separated out was filtered, washed with cold ethanol and recrystallized from acetic acid as white crystalline solid. IR spectrum (cm^{-1}) of **VIa** showed absorption bands at 3150 (NH), 2565 (—SH), 1690 (tertiary-amidic carbonyl), 1620, 1625 (cyclic and acyclic —C=N—) and 1365, 1160 (sulfonate ester moiety), 1110 (C=S). ^{1}H-NMR spectrum (δ/ppm) of (**VIa**) in ($CDCl_3$ + DMSO-d_6): 9.54 ppm ($C\underline{H}{=}N$), 7.85-6.80 ppm (m, 24H, 23 Ar—H and 1H for ylidene moiety) and 1.71 ppm (br., 1H, exchanged with D_2O, $S\underline{H}$).

4-Amino-3-[4- {4-(Z)-[p-(benzenesulfonyloxy)phenylmethylene]-5-oxo-1-phenyl-2-imidazolin-1-yl}phenyl]-5-methylthio-4H-1,2,4-triazole derivative (**VII**). Iodomethane (0.012 mol) was added portionwisely to a solution of (**V**) (5.9 g, 0.01 mol) in dry acetone (50 ml) containing anhydrous potassium carbonate (3 g) and the mixture was refluxed on steam bath for 8 h, cooled and filtered off. Removal of solvent under reduced pressure and subsequent addition of water afforded the thio-ether derivative (**VII**) which was filtered off, washed with water and recrystallized from ethanol as yellow crystals. IR spectrum (cm^{-1}) revealed absorption bands at 3470, 3380 (amino group), 1700 (tertiary-amidic CO), 1625 (—C=N—) and 1365, 1160 (sulfonate ester moiety).

1,2,4-Triazolo(3,4-b)-1,3,4-thiadiazine (**VIII**), *2-Ethoxycarbonyl-1,2,4-triazolo(3,4-b)-1,3,4-thiadiazine* (**IX**) *and 1,2,4-triazolo-(3,4-b)-1,3,4-thiadiazepine* (**X**) *fused ring systems*. *General procedures*: The N-Amino-triazole derivative (V) (5.9 g, 0.01 mol) was added to a suspension of anhydrous potassium carbonate (3 g) in dry acetone (50 ml). To this suspension, the corresponding halo ester (0.015 mol) was added with continuous stirring and the whole mixture was refluxed for 12 h. The resulting suspension was filtered off and excess solvent was distilled under reduced pressure. Addition of water (25 ml) afforded the desired products which were filtered off and recrystallized from methanol or ethanol. The IR spectra (cm^{-1}) of these products exhibited characteristic absorption bands near 1700 and 1665 cm^{-1} for cyclic tertiary and secondary amidic linkages respectively. ^{1}H-NMR spectrum (δ/ppm) of compound **IX** (DMSO-d_6) showed signals at 8.9 (br., 1H, —CON$\underline{H}$, exchanged with D_2O), 7.80-6.75 (m, 19H, 18H Ar—H and ylidene proton), 5.2 (s, 1H, C_2-H of triazolo-thiadiazine moiety), 4.4 (q, 2H, $C\underline{H}_2$-CH_3) and 1.95 ppm (t, 3H, CH_2-$C\underline{H}_3$).

4-[4-{4-(Z)-[p-(Benzenesulfonyloxy)phenylmethylene]-5-oxo-1-phenyl-2-imidazolin-1-yl}phenyl] 2-substituted 1,2,4-triazolo-(3,4-b)-1,3,4-thiadiazole derivatives (**XIIa,b**). *A. Direct method*: A mixture of the N-aminotriazole derivative (V) (5.9 g, 0.01 mol), carboxylic acid (0.01 mol) and phosphorus oxychloride (20 ml) was refluxed for 4–8 h and cooled. Distillation of excess oxychloride under reduced pressure gave a residue which was cautiously added to cold water (50 ml) and neutralized with dilute sodium bicarbonate solution to give a solid product that was filtered off, washed with water and recrystallized from ethanol or acetic acid as yellow to orange crystals in 62–64% yield. The IR spectrum of **XIIb** (cm^{-1}) showed absorption bands at 1700 (tertiary-amidic CO), 1625 (—C=N—) ant 1360, 1160 (sulfonate ester moiety). ^{1}H-NMR spectrum (δ/ppm) of the same derivative in ($CDCl_3$ + DMSO-d_6): revealed only a multiplet at 7.75–6.80 corresponding to the twenty four protons (23H Ar—H + ylidene proton).

Using acetic anhydride instead of acetic acid and phosphorus oxychloride in the above experiment afforded compound **XIIa** in 67% yield.

B. Indirect method for compound **XIIb**: 1. Formation of N-Benzoyl derivative (**XI**). A mixture of compound V (5.9 g, 0.01 mol) and benzoyl chloride (0.01 mol) in pyridine (15 ml) was stirred at ambient temperature for 5 h. The mixture was then poured onto crushed ice (100 g) and the precipitated benzoylamino derivative (**XI**) was filtered off, washed with water, dried and recrystallized from ethanol in 66% yield. IR spectrum (cm^{-1}) displayed absorption bands at 3150 (NH), 2570 (SH), 1700 (tertiary-amidic CO), 1685 (CONH), 1625 (—C=N—), 1365, 1160 (sulfonate ester group) and 1120 (—C=S).

2. Cyclization of **XI** to **XIIb**. The above N-Benzoyl derivative (0.7 g, 0.001 mol) was suspended in phosphorus oxychloride (10 ml) and boiled under reflux for 6 h. Working up of the reaction mixture, as in the case of the direct method, afforded the same product (**XIIb**) in 52% yield. A mixture melting point did not show a depression with an authentic sample prepared by method A.

Fungicidal Activity. All synthesized compounds were screened for fungitoxic activity against the rice blast pathogen Pyricularia oryzae and the brown leaf spot pathogen Helminthosporium oryzae by a standard method.[12] The experiments were performed in triplicate and the average percentage inhibition of spores at a concentration of 500 ppm of the synthesized products was determined and compared with the standard fungicide, Hinosan 50%, O-ethyl-S,S-diphenyl phosphodithioate. The screening data are reported in Table I. In general, most of the prepared compounds possessed a significant activity against the two pathogens. The highest fungitoxicity was observed for compound **IX** which showed 79% and 85% inhibition of spore germination against *P. oryzae* and *H. oryzae*, respectively at 500 ppm.

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