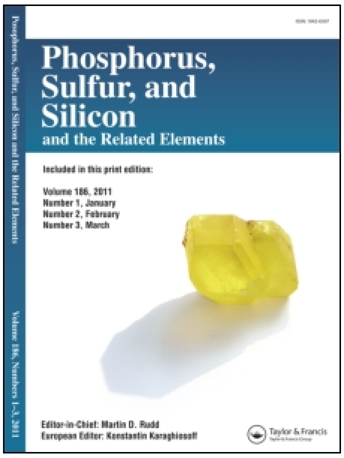

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SYNTHESIS OF SOME NEW 5-ARYLIDENE-3-BENZYL-2-ARYLIMINO-4-THIAZOLIDINONES

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SYNTHESIS OF SOME NEW 5-ARYLIDENE-3-BENZYL-2-ARYLIMINO-4-THIAZOLIDINONES

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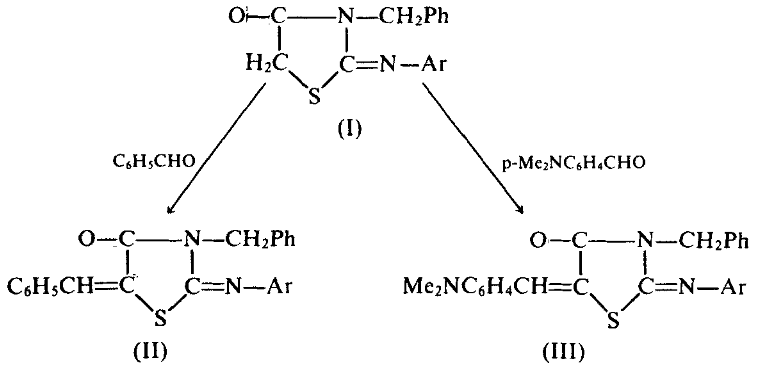
Some new 5-benzylidene derivatives (II) have been synthesized by condensing I with benzaldehyde in the presence of anhydrous sodium acetate and several 5-*p*-dimethylaminobenzylidene derivatives. (III) have been synthesized by condensing I with *p*-dimethylaminobenzaldehyde in the presence of pyridine. Some selected arylidene derivatives have been tested for their nematicidal, insecticidal, acaricidal and herbicidal activities.

5-Arylidene derivatives of 4-thiazolidinones have been reported to possess better antibacterial[1] and fungicidal activity[2,3] than the parent compounds. Several 3-aryl-substituted-5-arylidene-4-thiazolidinones have been found to be useful as ultrafiltering agents.[4,5]

Keeping these considerations in mind, the author has synthesized a number of new 5-benzylidene-3-benzyl-2-arylimino-4-thiazolidinones (II) and 5-(*p*-dimethylaminobenzylidene)-3-benzyl-2-arylimino-4-thiazolidinones (III) from 3- benzyl-2-arylimino-4-thiazolidinones (I).[6] The compounds of the type II were synthesized by condensing I with benzaldehyde in the presence of anhydrous sodium acetate and glacial acetic acid while that of type III were synthesized by condensing I with *p*-dimethylaminobenzaldehyde in the medium of pyridine. The compounds thus synthesized are described in Tables I and II.



RESULTS AND DISCUSSION

The structures of arylidene derivatives were confirmed by studying their N.M.R. and I.R. spectral data.

Comparing the N.M.R. spectra of benzylidene derivatives (II, Ar=o-phenetyl) with the parent 4-thiazolidinones (I, Ar=o-phenetyl), it was observed that the sharp singlet at $\delta 3.86$ for active methylene protons (CH_2-CO) at position 5 in the

TABLE I

5-Benzylidene-3-benzyl-2-arylimino-4-thiazolidinones (II)

Compound No.	Ar	Molecular formula	Yield %	m.p. °C	Found (%)			Required (%)		
					C	H	N	C	H	N
1.	p-Tolyl	$C_{24}H_{20}N_2OS$	66	127	75.26	5.48	7.06	75.00	5.21	7.29
2.	p-Anisyl	$C_{24}H_{20}N_2O_2S$	70	70	72.18	5.16	6.82	72.00	5.00	7.00
3.	o-Phenetyl[a]	$C_{25}H_{22}N_2O_2S$	88	127	72.28	5.44	6.80	72.46	5.31	6.76
4.	p-Fluorophenyl	$C_{23}H_{17}FN_2OS$	85	85	70.93	4.26	7.48	71.13	4.38	7.22
5.	o-Chlorophenyl	$C_{23}H_{17}ClN_2OS$	91	103	68.47	4.04	7.11	68.23	4.20	6.92
6.	p-Chlorophenyl	$C_{23}H_{17}ClN_2OS$	86	67	68.41	4.16	7.19	68.23	4.20	6.92
7.	p-Iodophenyl	$C_{23}H_{17}IN_2OS$	90	126	55.56	3.66	5.37	55.64	3.43	5.64
8.	2,4-Dichlorophenyl	$C_{23}H_{16}Cl_2N_2OS$	80	126	62.64	3.89	6.51	62.87	3.64	6.40
9.	o-Hydroxyphenyl	$C_{23}H_{18}N_2O_2S$	77	122	71.36	4.86	7.37	71.50	4.66	7.25
10.	m-Hydroxyphenyl	$C_{23}H_{18}N_2O_2S$	77	164	71.25	4.82	7.16	71.50	4.66	7.25
11.	p-Hydroxyphenyl	$C_{23}H_{18}N_2O_2S$	73	208–10[b]	71.38	4.48	7.54	71.50	4.66	7.25
12.	1-Naphthyl	$C_{27}H_{20}N_2OS$	63	114	76.93	4.92	6.94	77.14	4.76	6.67
13.	2-Pyridyl	$C_{22}H_{17}N_3OS$	72	182	71.33	4.43	11.12	71.16	4.58	11.32
14.	3-Pyrazolyl	$C_{20}H_{16}N_4OS$	91	188–90[b]	66.48	4.67	15.70	66.67	4.44	15.55
15.	Cyclohexyl	$C_{23}H_{24}N_2OS$	99	101[b]	73.26	6.51	7.29	73.40	6.38	7.45

[a] N.M.R. ($CDCl_3$)δ: 1.33 (t, 3H, $J = 7.5$ Hz, OCH_2CH_3—o), 4.05 (q, 2H, $J = 7.5$ Hz, OCH_2CH_3—o), 5.10 (s, 2H, $C_6H_5CH_2$), 7.25 (complex multiplet, 14 H, aromatic protons) and 7.77 (s, 1H, $C_6H_5—CH{=}C<$). I.R. (KBr) cm^{-1}: 2950, 2885 (CH_2), 1735 (C=O), 1665 (C=N), 1620 (aliphatic C=C) and 755 (C—5).

[b] Decomposed.

TABLE II

5-(p-Dimethylaminobenzylidene)-3-benzyl-2-arylimino-4-thiazolidinones (III)

Compound No.	Ar	Molecular formula	Yield %	m.p. °C	Found (%)			Required (%)		
					C	H	N	C	H	N
16.	p-Tolyl	$C_{26}H_{25}N_3OS$	69	180	73.22	6.07	9.67	73.07	5.85	9.84
17.	p-Anisyl	$C_{26}H_{25}N_3O_2S$	67	195	70.19	5.34	9.75	70.43	5.64	9.48
18.	p-Fluorophenyl	$C_{25}H_{22}FN_3OS$	66	102	69.88	4.96	9.02	69.60	5.11	9.74
19.	p-Chlorophenyl	$C_{25}H_{22}ClN_3OS$	75	222–24[b]	67.28	5.18	9.13	67.04	4.92	9.38
20.	p-Bromophenyl	$C_{25}H_{22}BrN_3OS$	72	230	60.86	4.56	8.79	60.97	4.47	8.54
21.	p-Iodophenyl	$C_{25}H_{22}IN_3OS$	77	>250	55.47	3.86	8.07	55.66	4.08	7.79
22.	2,4-Dichlorophenyl	$C_{25}H_{21}Cl_2N_3OS$	87	>250	62.09	4.59	8.81	62.24	4.36	8.71
23.	2,5-Dichlorophenyl	$C_{25}H_{21}Cl_2N_3OS$	78	>250	62.35	4.66	8.46	62.24	4.36	8.71
24.	m-Hydroxyphenyl	$C_{25}H_{23}N_3O_2S$	69	218	68.94	5.47	9.97	69.13	5.36	9.79
25.	4-Hydroxy-2-methyl-phenyl	$C_{26}H_{25}N_3O_2S$	72	182	70.26	5.48	9.70	70.43	5.64	9.48
26.	1-Naphthyl	$C_{29}H_{25}N_3OS$	68	135	74.88	5.63	9.18	75.16	5.40	9.07
27.	2-Pyridyl[a]	$C_{24}H_{22}N_4OS$	72	>250	69.39	5.53	13.67	69.56	5.31	13.53
28.	3-Pyrazolyl	$C_{22}H_{21}N_5OS$	71	>250	65.32	5.07	17.62	65.51	5.21	17.37
29.	Cyclohexyl	$C_{25}H_{29}N_3OS$	69	55	71.35	7.19	10.17	71.60	6.92	10.02

[a] N.M.R. ($CDCl_3$) δ: 3.07 [s, 6H, $(CH_3)_2NC_6H_4$-], 5.32 (s, 2H, $C_6H_5CH_2$), 7.27 (complex multiplet, 13H, aromatic protons) and 7.80 (s, 1H, $>NC_6H_4-CH{=}C<$). I.R. (KBr)cm^{-1}: 2920, 2850 (CH_2), 1700 (C=O), 1620 (aliphatic C=C), 1610 (C=N) and 750 (C—S).

[b] Decomposed.

parent 4-thiazolidinone is absent in the N.M.R. spectrum of the compound (II, Ar=o-phenetyl) due to condensation. Further, a singlet at δ7.77 for methine proton ($C_6H_5CH{=}C<$) is observed in the N.M.R. spectrum of the compound (II, Ar=o-phenetyl). In addition to this, I.R. spectrum of the compound (II, Ar=o-phenetyl) showed the characteristic absorption peak at 1620 cm^{-1} for an aliphatic C=C bond. These observations support the structure II assigned to 5-benzylidene derivatives. The elemental analyses of all these compounds also agree with the assigned structures.

Similarly comparing *p*-dimethylaminobenzylidene derivatives (III, Ar=2-pyridyl) with that of the parent 4-thiazolidinones (I, Ar=2-pyridyl), it was found that a sharp singlet at δ3.68 for active methylene protons (CH_2CO) at position 5 in the parent 4-thiazolidinone is found absent on account of condensation. The *p*-dimethylaminobenzylidene derivative (III, Ar=2-pyridyl) showed an additional singlet at δ7.80 for methine proton ($Me_2NC_6H_4CH{=}C<$). In addition to this, the I.R. spectrum of the compound (III, Ar=2-pyridyl) showed a characteristic absorption peak at 1620 cm^{-1} for an aliphatic C=C bond. These observations support the structure III assigned to 5-*p*-dimethylaminobenzylidene derivatives. The elemental analyses of all these compounds also agree with the assigned structures.

EXPERIMENTAL

All the melting points have been observed in open capillary tubes and are uncorrected. The N.M.R. spectra were recorded on a Varian A-60D in $CDCl_3$ with TMS as the internal standard. The I.R. spectra were taken on Perkin-Elmer 621 spectrophotometer in the form of KBr discs.

Different 3-benzyl-2-arylimino-4-thiazolidinones required for the synthesis of different arylidene derivatives were synthesized by the method of Dains *et al.*[7] as modified by Rao[8-10] by condensing various 1-benzyl-3-aryl-2-thioureas[11] with monochloroacetic acid. Different 1-benzyl-3-aryl-2-thioureas were synthesized by reacting different amines with benzyl isothiocyanate.

5-Benzylidene-3-benzyl-2-arylimino-4-thiazolidinones (II) A mixture of 3-benzyl-2-arylimino-4-thiazolidinone (II) (0.01 M), benzaldehyde (0.06 M), anhydrous sodium acetate (0.06 M) and glacial acetic acid (50 ml) was refluxed on an asbestos wire-gauze for 2 hrs. After cooling the reaction mixture, excess of water was added to it and the reaction mixture was kept aside until the product separated as a crystalline solid. It was separated by filtration. It was washed several times with hot water, dried and recrystallized from absolute ethanol. The compounds thus prepared are listed in Table I along with their relevant data.

5-p-Dimethylaminobenzylidene-3-benzyl-2-arylimino-4-thiazolidinones (III) 3-Benzyl-2-arylimino-4-thiazolidinones (0.01 M) and *p*-dimethylaminobenzaldehyde (0.03 M) were refluxed in pyridine (25 ml) on an asbestos wire-gauze for about 5 hrs. After the completion of the reaction, the reaction mixture was poured into excess of water and kept aside until the product separated as a crystalline solid. The separated solid was filtered, washed several times with dilute hydrochloric acid and excess of water, dried and recrystallized from an alcohol-chloroform mixture. The compounds thus synthesized are listed in Table II along with their relevant data.

Biological Activity

Compounds 6, 13, 14, 20, 27 and 28 were screened for their nematicidal, insecticidal, acaricidal and herbicidal activities. Surprisingly none of the compounds showed any activity.

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