

spectral analyses. The IR spectroscopic data show characteristic absorption bands in the region 3100 to 3000 cm^{-1} which were assigned to C-H stretching mode of pyrimidine ring. The bands in the region 1600 to 1500 cm^{-1} are due to interaction between C=C and C=N vibrations of the ring. The NMR spectra of pyrimidines showed a pyrimidyl proton (C₅-H) in the range δ 6.40–6.80 and aromatic protons in the range δ 6.60–8.40.

All substituted phenacyldimethylsulphonium bromides (1) were prepared by heating *p*-substituted phenacyl bromide with dimethylsulphide in acetone as reported in the literature^{1,2,7-9}.

Preparation of 2,4,6-triarylpyrimidines (5a-l)

A mixture of 3 mmoles of *p*-substituted phenacyldimethylsulphonium bromide (1), 6 mmoles of aromatic aldehyde (2) and 3 g of ammonium acetate in 50 ml of glacial acetic acid was stirred at room temperature for 6–10 h. The mixture was then refluxed for 4–8 h and left at room temperature overnight. It was then poured into ice-cold water (50 ml) with constant stirring. The solid mass precipitated was filtered and washed twice with water and then with methanol. The product, on crystallization with appropriate solvents, gave crystalline 2,4,6-triarylpyrimidine (5a-l) in 40–80% yield.

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SYNTHESIS OF THIOSEMICARBAZIDES, TRIAZOLES, THIADIAZOLES AND OXADIAZOLES

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A broad spectrum of biological activity, including antibacterial, antifungal, anticonvulsant, fungicidal, anti-inflammatory and tranquilizing effects, is reported to be associated with thiosemicarbazides, triazoles, thiadiazoles and oxadiazoles¹⁻⁶. Therefore it was of interest to synthesize 4,4'-diphenyl-bis-pimelyl/suberyl/sebacyl/azelyl thiosemicarbazides (IIa-d), bis(4-phenyl-5-mercapto-1,2,4-triazol-3-yl) alkanes (IIIa-d), bis(5-phenylamino-1,3,4-thiadiazol-2-yl) alkanes (IVa-d), and bis(5-mercapto-1,3,4-oxadiazol-2-yl) alkanes (Va-d) from pimelic, suberic, sebacic and azelaic acids. Pimelic and azelaic acids were obtained by the oxidation of 7-hydroxyheptanal and azelaic acid aldehyde, the periodate oxidation⁷ products of aleuritic acid (9,10,16-trihydroxypalmitic acid), the major constituent acid of shellac.

The thiosemicarbazides IIa-d were obtained by the condensation of methanolic solution of the acid hydrazides (Ia-d) with phenylisothiocyanate at steam-bath temperature.

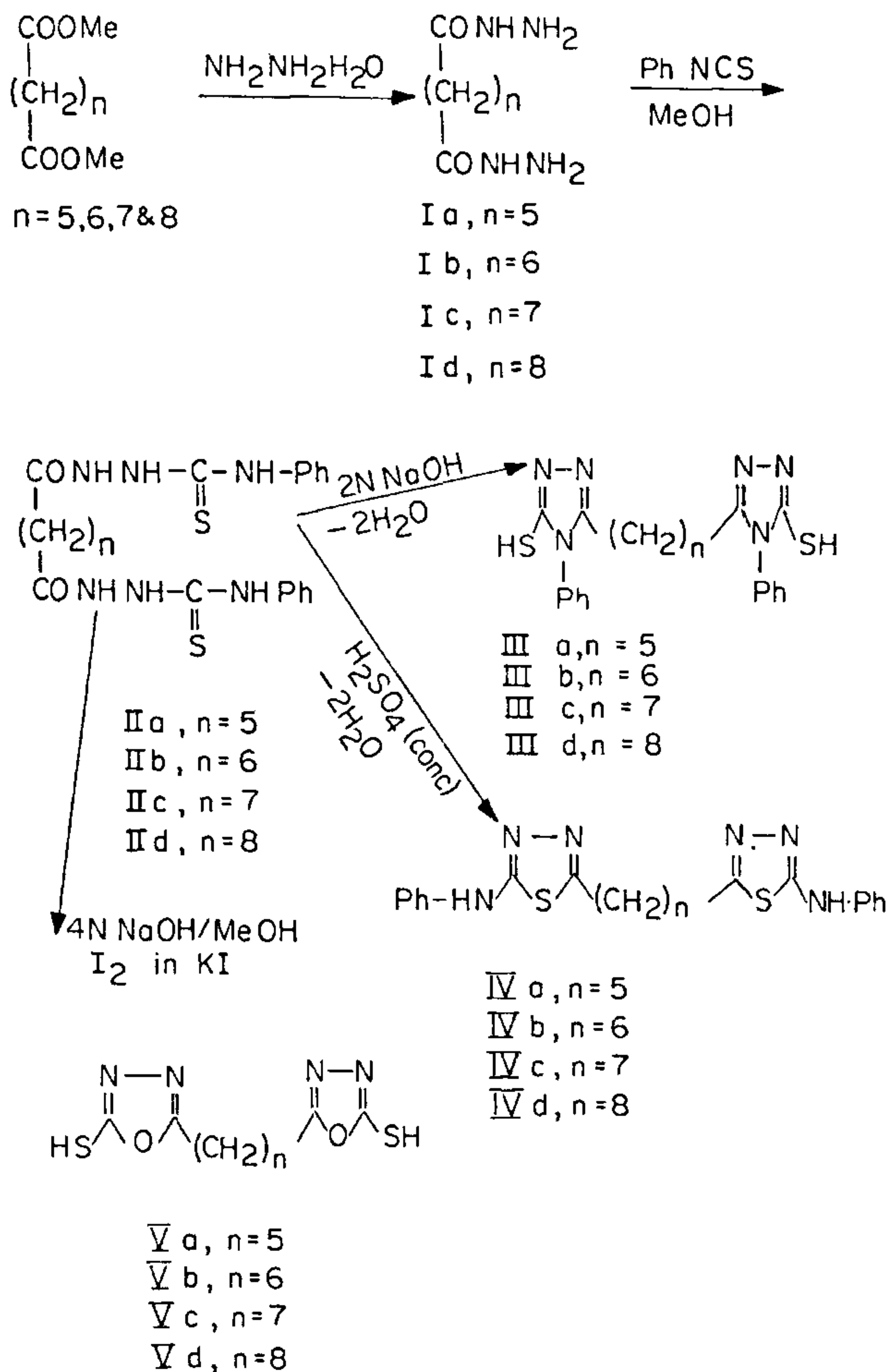
Bis(4-phenyl-5-mercapto-1,2,4-triazol-3-yl) alkanes IIIa-d were obtained by the cyclization of IIa-d with 2 N NaOH at reflux temperature. Treatment of IIa-d with ice-cold conc. H₂SO₄ at room temperature for 2 h afforded bis-thiadiazoles IVa-d, while thiosemicarbazide IIa-d in 4 N NaOH when heated under reflux in methanol and iodine in KI solution afforded bis-oxadiazoles Va-d.

4,4'-Diphenyl-bis-pimelyl/suberyl/sebacyl/azelyl thiosemicarbazides (IIa-d)

Methanolic solution of acid hydrazide (I, 0.1 mol) and phenylisothiocyanate (0.21 mol) was refluxed for 4 h. It was then cooled, and the solid that separated out was filtered, washed, dried and crystallized. Physical data are reported in table 1.

Bis(4-phenyl-5-mercapto-1,2,4-triazol-3-yl) alkanes (IIIa-d)

These compounds were prepared according to the method of Mishra and Bahel⁸. The characterization data are given in table 2.



Scheme

Bis(5-phenylamino-1,3,4-thiadiazol-2-yl) alkanes (IVa-d)

The titled compounds were prepared following the procedure reported in the literature⁶. The data are reported in table 3.

Bis(5-mercapto-1,3,4-oxadiazol-2-yl) alkanes (Va-d)

Thiosemicarbazide (1 g) in 4 N NaOH (5 ml) was heated under reflux in methanol (25 ml) and then iodine (2.5 g) in 10 ml of KI (3.2 g) solution was added to it till the colour of iodine persisted. The

Table 1 Physicochemical data for thiosemicarbazides

Compound	<i>n</i>	Yield (%)	m.p.* (°C)	Mol. formula	Analysis (%)	
					N Found (Cald.)	S Found (Cald.)
IIa	5	80	87-89	C ₂₁ H ₂₆ O ₂ N ₆ S ₂	18.21 (18.34)	14.00 (13.97)
IIb	6	70	177-78	C ₂₂ H ₂₈ O ₂ N ₆ S ₂	17.62 (17.79)	13.51 (13.55)
IIc	7	75	172-73	C ₂₃ H ₃₀ O ₂ N ₆ S ₂	17.22 (17.28)	13.00 (13.16)
IId	8	72	92-93	C ₂₄ H ₃₂ O ₂ N ₆ S ₂	16.78 (16.80)	12.62 (12.80)

*All the compounds were crystallized from MeOH.

IR (KBr): 3200-3190 (-NH), 1680-1675 (secondary-CONH), 1180-1175 (-C=S) cm⁻¹.

Table 2 Physicochemical data for triazoles

Compound	<i>n</i>	Yield (%)	m.p.* (°C)	Mol. formula	Analysis (%)	
					N Found (Requires)	S Found (Requires)
IIIa	5	75	140-42	C ₂₁ H ₂₂ N ₆ S ₂	19.84 (19.90)	14.92 (15.16)
IIIb	6	70	243-45	C ₂₂ H ₂₄ N ₆ S ₂	19.20 (19.26)	14.60 (14.67)
IIIc	7	68	228-30	C ₂₃ H ₂₆ N ₆ S ₂	18.56 (18.66)	13.93 (14.22)
IIId	8	60	102-3	C ₂₄ H ₂₈ N ₆ S ₂	17.90 (18.10)	13.70 (13.79)

*The compounds were crystallized from EtOH.

IR (KBr): 3200-3150 (-NH), 1500-1490 (-C=N), 1180-1175 (C=S) cm⁻¹.

PMR: δ 7.3 (s, NH, Ar-H), 2.15-3.15 (t, methylene protons).

Table 3 Physicochemical data for thiadiazoles

Compound	<i>n</i>	Yield (%)	m.p.* (°C)	Mol. formula	Analysis (%)	
					N Found (Requires)	S Found (Requires)
IVa	5	70	87-89	C ₂₁ H ₂₂ N ₆ S ₂	19.81 (19.90)	14.95 (15.16)
IVb	6	68	226-28	C ₂₂ H ₂₄ N ₆ S ₂	19.00 (19.26)	14.53 (14.67)
IVc	7	65	183-85	C ₂₃ H ₂₆ N ₆ S ₂	18.50 (18.66)	14.20 (14.22)
IVd	8	63	105-6	C ₂₄ H ₂₈ N ₆ S ₂	17.92 (18.10)	13.72 (13.79)

*Solvent used for crystallization was MeOH.

IR (KBr): 3320-3300 (secondary-NH), 1500-1490 (conjugated cyclic system -C=N), 1175-1170 (-C=S) cm⁻¹.

PMR: δ 6.5-6.7 (s, -NH), 7.1-7.7 (m, Ar-H).

Table 4 Physicochemical data for oxadiazoles

Compound	n	Yield (%)	m.p.* (°C)	Mol. formula	Analysis (%)	
					N Found (Requires)	S Found (Requires)
Va	5	68	240(d)	C ₉ H ₁₂ O ₂ N ₄ S ₂	20.60 (20.58)	22.90 (23.52)
Vb	6	65	233-35	C ₁₀ H ₁₄ O ₂ N ₄ S ₂	19.38 (19.58)	22.30 (22.37)
Vc	7	58	180	C ₁₁ H ₁₆ O ₂ N ₄ S ₂	18.45 (18.66)	21.25 (21.33)
Vd	8	60	112-13	C ₁₂ H ₁₈ O ₂ N ₄ S ₂	17.63 (17.83)	20.20 (20.38)

*Compounds crystallized from EtOH.

IR (KBr): 3150-3100 (-NH), 1510-1500 (-C=N), 1175-1170 (C=S) cm⁻¹.

mixture was then concentrated and cooled, and the solid which separated was filtered, dried and crystallized. The data are given in table 4.

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SYNTHESIS, CHARACTERIZATION AND ANTIMICROBIAL ACTIVITY OF THIOMALATES OF Ag(I), Hg(II) AND Cd(II)

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THIOMALIC acid (TMA) is a versatile ligand with a 'soft' sulphur of a sulphhydryl group and 'hard' oxygens of two carboxylate groups. Its complexes with many metal ions have been reported in solution¹⁻⁶, though only a few of them have been isolated and characterized⁷⁻¹⁰. TMA is also a biologically important compound which has been shown to serve as an antidote against cadmium, mercury and arsenic poisoning¹¹; its complexes with some metal ions have been recommended in the treatment of various disorders¹²⁻¹⁴. In this context it was thought desirable to synthesize and characterize some more complexes and also determine their antimicrobial activity. In this paper such studies on metal thiomalates of Ag(I), Hg(II) and Cd(II) are reported.

Metal acetates and nitrates and thiomalic acid used were of analytical reagent grade. IR spectra (4000-200 cm⁻¹) were recorded on a NICOLET-DX in KBr-CsI pellet/nujol mull. ¹H NMR spectra were recorded in a JEOL FT NMR Fx 90Q spectrometer in DMSO-d₆.

Thermogravimetric analysis was carried out on a fabricated instrument. Heating rate was maintained at 10°C/minute.