

complexes were formed, with stability constants $\log B_{10} = 3.60$ and $\log B_{20} = 5.86$. Deford and Hume's⁵ method was applied to determine the stability constants of successive complexes.

In(III)-tartrate system

The $E_{\frac{1}{2}}$ vs $\log[\text{Tart}^{-2}]$ curve gave a straight line indicating the formation of one complex species and hence the method of Lingane⁶ was adopted for the evaluation of stability constants and co-ordination number. The stability constant of the simple complex formed was found to be $\log B = 3.4$.

Mixed In(III)-1-methylimidazole-tartrate system

The 1-methylimidazole concentration was varied from 0.02 to 0.20 M and that of tartrate was kept constant at 0.1 M. The $E_{\frac{1}{2}}$ values were greater than those obtained in the absence of tartrate, thereby indicating the formation of mixed complexes. The system was studied at another concentration of tartrate (0.20 M). To determine the values of the stability constants of mixed-ligand complexes, the method of Schaap and McMasters⁷ was applied. The polarographic characteristics and function $F_{ij}(X)$ of the mixed complexes at fixed $[\text{Tart}^{-2}]$ (0.1 and 0.2 M) are presented in tables 1 and 2.

Table 1 *In(III)-1-methylimidazole-tartrate system, $[\text{In(III)}] = 1 \times 10^{-3}$ M and $[\text{Tart}^{-2}] = 0.1$ M (fixed)*

[1-Melm]	$-E_{\frac{1}{2}}$	$F_{00}(X) \cdot 10^{-1}$	$F_{10}(X) \cdot 10^{-3}$	$F_{20}(X) \cdot 10^{-5}$
0.00	0.510			
0.02	0.520	3.95		
0.04	0.530	21.53	3.98	
0.08	0.540	179.55	22.00	26.59
0.10	0.550	339.00	32.97	28.00
0.15	0.560	1504.98	99.87	41.98
0.20	0.570	2139.99	106.79	24.89

$\mu = 2.0$ NaNO₃, pH 7.4, temp. 25°C.

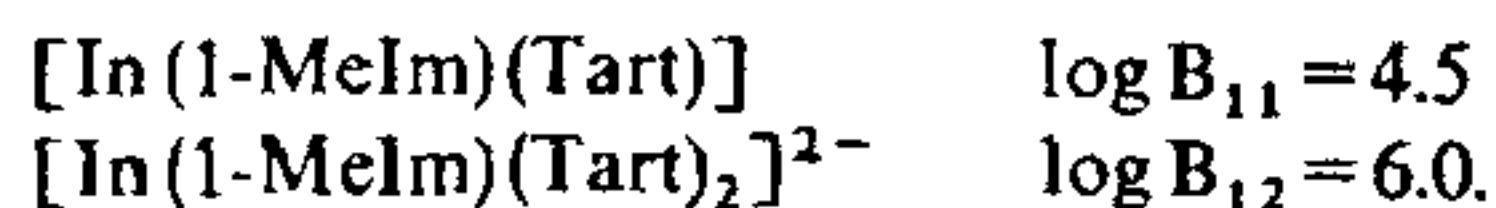
Table 2 *In(III)-1-methylimidazole-tartrate system, $[\text{In(III)}] = 1 \times 10^{-3}$ M and $[\text{Tart}^{-2}] = 0.2$ M (fixed)*

[1-Melm]	$-E_{\frac{1}{2}}$	$F_{00}(X) \cdot 10^{-1}$	$F_{10}(X) \cdot 10^{-3}$	$F_{20}(X) \cdot 10^{-5}$
0.00	0.510			
0.02	0.530	2.09		
0.04	0.540	6.98	13.31	23.20
0.08	0.550	35.31	42.00	47.56
0.10	0.560	72.00	70.00	58.00
0.15	0.570	339.87	229.00	94.99
0.20	0.580	960.99	279.98	72.98

$\mu = 2.0$ NaNO₃, pH 7.4, temp. 25°C.

The stability constants were calculated from the analysis of $F_{ij}(X)$ functions.

The values are reproducible to $\pm 4\%$. Two mixed complexes as noted below are formed:



The value of the mixing constant K_M is +0.7 (ref. 8, 9). The positive value of the mixing constant shows that the mixed complex $[\text{In(1-Melm)(Tart)}]$ is somewhat more stable than the simple biscomplexes of In(III) with 1-methylimidazole and tartrate.

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REACTION OF SOME *p*-SUBSTITUTED PHENACYLDIMETHYLSULPHONIUM BROMIDES WITH AROMATIC ALDEHYDES: SYNTHESIS OF 2,4,6-TRIARYLPYRIMIDINES

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SULPHONIUM salts have gained considerable importance in the synthesis of a large variety of heterocyclic compounds, viz. substituted pyridines^{1,2}, indoles³, tetrazines⁴, azaridines⁵, etc. But they have not been utilized in the synthesis of 2,4,6-triarylpymidines. Work described here involves aza ring closure with condensation of sulphonium salts

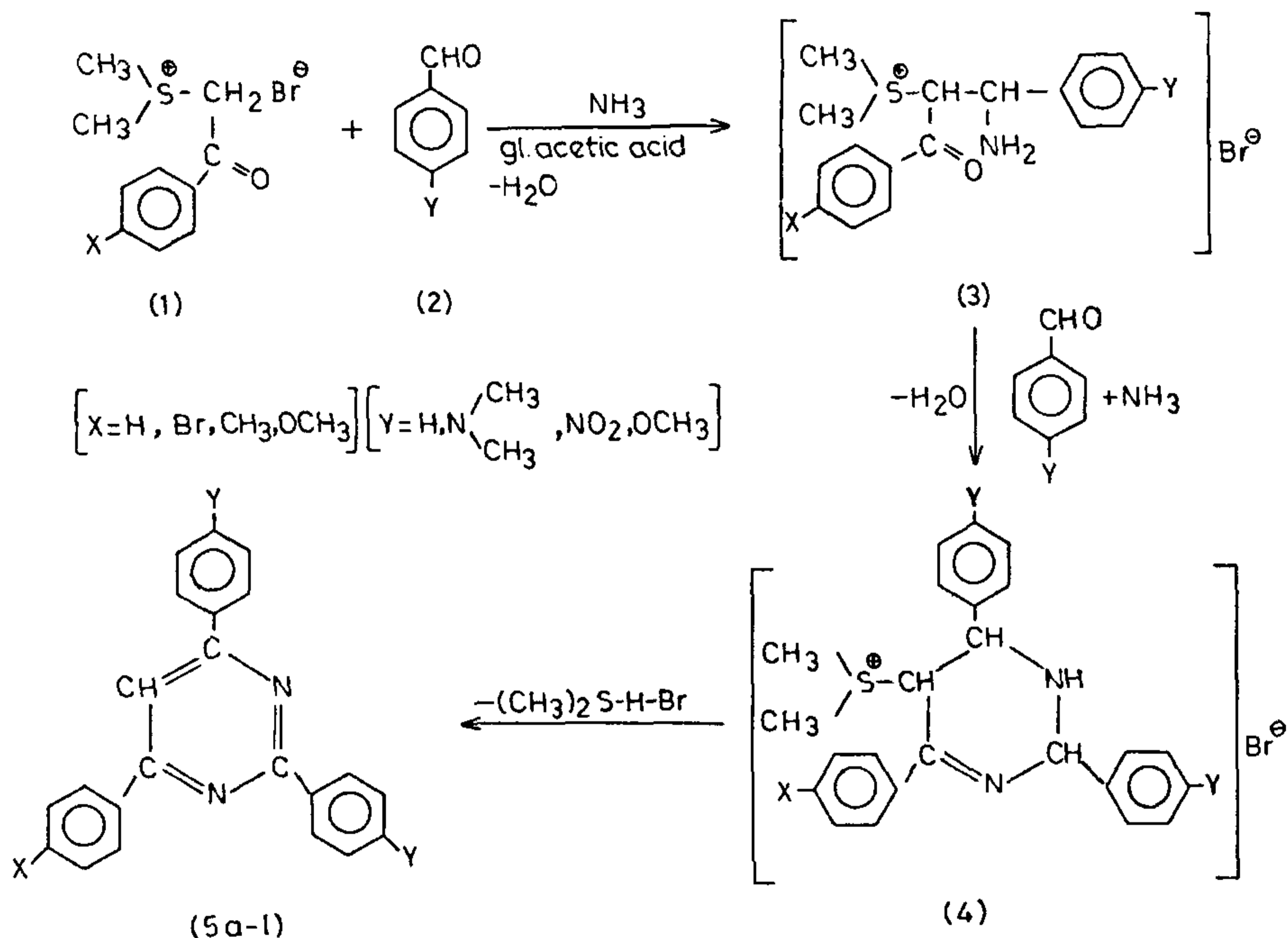
with aromatic aldehydes in the presence of glacial acetic acid and liquid ammonia, leading to the synthesis of 2,4,6-triarylpyrimidines (5a-l).

Heating a mixture of *p*-substituted phenacyldimethylsulphonium bromide with benzaldehyde carrying electron attracting and donating substituents at the *para* position in the presence of glacial acetic acid and liquid ammonia at reflux temperature for 4–5 resulted in 2,4,6-triarylpyrimidine with 40–80% yield (scheme 1).

The course of reaction involves a Mannich-type

reaction. The methylene group of the salt (1) with aromatic aldehyde (2) in the presence of liquid ammonia forms a Mannich base-sulphonium salt (3), which, in turn, undergoes condensation with another molecule of benzaldehyde in the presence of ammonia to form a sulphonium salt intermediate (4). The latter then undergoes elimination of dimethylsulphonium hydrobromide and H₂ to form 2,4,6-triarylpyrimidine (5a-l).

Some 2,4,6-triarylpyrimidines (5a-l) synthesized by the above route gave satisfactory elemental and



5a.	X: 4-H	Y: 4-H	g:	X: 4-CH ₃	Y: 4-H
b.	X: 4-H	Y: 4-N(CH ₃) ₂	h:	X: 4-CH ₃	Y: 4-NO ₂
c.	X: 4-H	Y: 4-NO ₂	i:	X: 4-CH ₃	Y: 4-N(CH ₃) ₂
d.	X: 4-Br	Y: 4-H	j:	X: 4-OCH ₃	Y: 4-NO ₂
e.	X: 4-Br	Y: 4-NO ₂	k:	X: 4-OCH ₃	Y: 4-N(CH ₃) ₂
f.	X: 4-Br	Y: 3,4-OCH ₃	l:	X: 4-OCH ₃	Y: 4-H

Scheme 1.

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.