

IR: 1695 (ketone), 1590 (aromatic), 820 ( $-\text{CH}=\text{C}<$ ). PMR ( $\text{CDCl}_3$ ): 1.06 (4H, s overlapping a multiplet, one of the cyclopropanemethyls and  $\text{C}_3$  H), 1.26 (3H, s, another cyclopropanemethyl), 1.48 (1H, m,  $\text{C}_1$  H), 2.08 (3H, s, vinylmethyl), 5.26, 5.54 (1H, d each,  $J=9$  Hz each, olefinic H of *Z* and *E* isomers respectively), 7.30 (4H, s, aromatic H on  $\text{C}_1$  side chain) and 7.42, 7.82 (4H, d each,  $J=9$  Hz each, aromatic H of benzoyl group on  $\text{C}_3$  side chain).

Ozonolysis of VIII, followed by oxidative work-up (Jones reagent) and esterification ( $\text{CH}_2\text{N}_2$ ) afforded a solid ketoester (62%), m.p.  $61^\circ\text{C}$  (pet. ether),  $\text{C}_{15}\text{H}_{17}\text{O}_3\text{Cl}$ ,  $[\alpha]_{\text{D}}^{30} + 65^\circ$  ( $c$ , 0.6,  $\text{CHCl}_3$ ), identified as methyl 1*S*-*cis*-2,2-dimethyl-3-(2-*p*-chlorophenyl-2-oxoethyl)cyclopropanecarboxylate (IX) by comparison of spectral properties<sup>1</sup>.

Phosphorus pentachloride reaction<sup>3</sup> on ketoester (IX) followed by purification over silicic acid gave vinylchloroester (XI, 55%),  $\text{C}_{15}\text{H}_{16}\text{O}_2\text{Cl}_2$ .  $[\alpha]_{\text{D}}^{30} + 95.5^\circ$  ( $c$ , 0.5,  $\text{CHCl}_3$ ). IR: 1726 ( $\text{C}=\text{O}$ ), 1595 (aromatic). PMR ( $\text{CDCl}_3$ ): 1.26, 1.31 (6H, s each, cyclopropanemethyls), 1.8 (1H, d,  $J=8$  Hz,  $\text{C}_1$  H), 2.28 (1H, t,  $J=8$  Hz,  $\text{C}_3$  H), 3.53, 3.6 (3H, s each, estermethyls of *E* and *Z* isomers), 5.33, 6.43 (1H, d each,  $J=8$  Hz each, olefinic H of *Z* and *E* isomers respectively) and 7.06–7.44 (4H, m, aromatic H of *E* and *Z* isomers).

Treatment of chloroester (XI) for epimerization<sup>4</sup> and dehydrohalogenation with *t*-BuOK (6 mol) in *t*-BuOH, under reflux, gave a mixture of products, separated into acidic and neutral parts. The acid part on esterification ( $\text{CH}_2\text{N}_2$ ) and purification by chromatography (silicic acid) afforded a pure liquid (9%),  $\text{C}_{15}\text{H}_{15}\text{O}_2\text{Cl}$ ,  $[\alpha]_{\text{D}}^{30} + 89^\circ$  ( $c$ , 0.5,  $\text{CHCl}_3$ ) as one of the products, identified as methyl (+)-1*R*-*trans*-2,2-dimethyl-3-(2-*p*-chlorophenylethynyl)cyclopropanecarboxylate (XII) by spectral properties<sup>1</sup>. The neutral portion on purification gave TLC-pure solid (21%), m.p.  $80^\circ\text{C}$  (pet. ether),  $\text{C}_{18}\text{H}_{21}\text{O}_2\text{Cl}$ ,  $[\alpha]_{\text{D}}^{30} + 76^\circ$  ( $c=0.6$ ,  $\text{CHCl}_3$ ) as one of the products, identified as *t*-butyl (+)-1*R*-*trans*-2, 2-dimethyl-3-(2-*p*-chlorophenylethynyl) cyclopropanecarboxylate (XIII) by spectral properties<sup>1</sup>.

The *cis*-hydroxy ester (X), which is an important intermediate for ketoester (IX) was also prepared by ozonolysis of unsaturated acetate (VI), followed by decomposition<sup>5</sup> of the resulting ozonide with NaOH/MeOH and esterification of resulting acid.

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## CO-ORDINATION COMPLEXES OF DIORGANOTIN

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SOME work on co-ordination complexes of first row transition metals with a variety of macrocycles has been reported from this laboratory<sup>1-5</sup>. The present communication reports the synthesis and characterization of six complexes involving diorganotin as Lewis acids. The complexes, on the basis of analytical, conductance and IR studies, have been assigned octahedral structures in which the ligands occupy four planar and the phenyl groups two trans-axial positions around the tin atom.

The organotin compounds and the primary ligand *N,N*-bis(2,4-dinitrophenyl) ethylenediamine ( $\text{L}_1$ ) have been prepared by reported methods<sup>6,7</sup>. The ligand  $\text{L}_2$  has been obtained by reducing  $\text{L}_1$  using Raney nickel and hydrazine hydrate, while condensation of  $\text{L}_2$  with acetylacetone in 1:1 ratio gives the macrocyclic ligand  $\text{L}_3$ .

The complexes have been prepared by stirring 0.01 M diorganotin derivatives with 0.01 M of different ligands in absolute methanol for about 8 h. They were crystallized out using petroleum ether and purified by running over TLC plates, dried and analysed. Tin was estimated using the reported method. Semimicro-estimation of C, H and N and recording of infrared spectra mullied in nujol in the range  $4000-200\text{ cm}^{-1}$ , were carried out at CDRI, Lucknow. The molar conductance was measured in DMSO over a direct reading conductivity bridge.

27 August 1988

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Table 1 Analytical and molar conductance data for the complexes

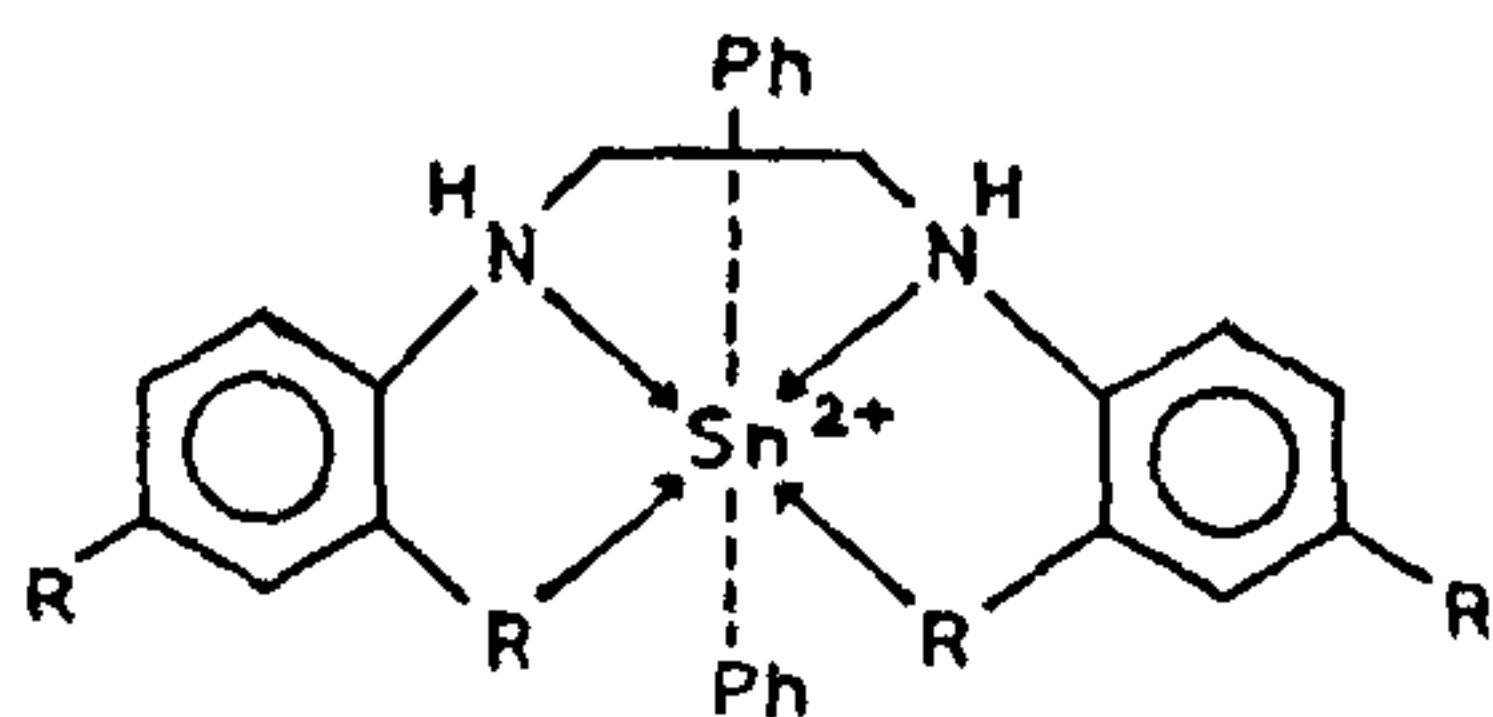
Compound	% Sn	% C	% H	% N	Molar conductance in DMSO ( $S\text{ cm}^2\text{ mol}^{-1}$ )
$[\text{Sn}(\text{L}_1)](\text{ClO}_4)_2$	13.28 (13.77)	35.80 (36.11)	2.98 (2.55)	9.01 (9.72)	38.95
$[\text{Sn}(\text{L}_1)](\text{BF}_4)_2$	14.51 (14.22)	36.92 (37.29)	2.04 (2.63)	10.62 (10.03)	51.06
$[\text{Sn}(\text{L}_2)](\text{ClO}_4)_2$	15.71 (15.99)	40.61 (41.93)	3.58 (4.03)	11.71 (11.28)	59.00
$[\text{Sn}(\text{L}_2)](\text{BF}_4)_2$	16.48 (16.59)	43.02 (43.51)	4.62 (4.18)	11.52 (11.71)	48.50
$[\text{Sn}(\text{L}_3)](\text{ClO}_4)_2$	14.64 (14.81)	45.81 (46.33)	4.81 (4.23)	10.96 (10.46)	62.20
$[\text{Sn}(\text{L}_3)](\text{BF}_4)_2$	15.02 (15.24)	47.68 (47.63)	4.89 (4.35)	10.09 (10.76)	48.50

$\text{L}_1 = \text{C}_{14}\text{H}_{12}\text{N}_6\text{O}_8$ ;  $\text{L}_2 = \text{C}_{14}\text{H}_{20}\text{N}_6$ ;  $\text{L}_3 = \text{C}_{19}\text{H}_{24}\text{N}_6$ ; Numbers in parentheses are % calcd.

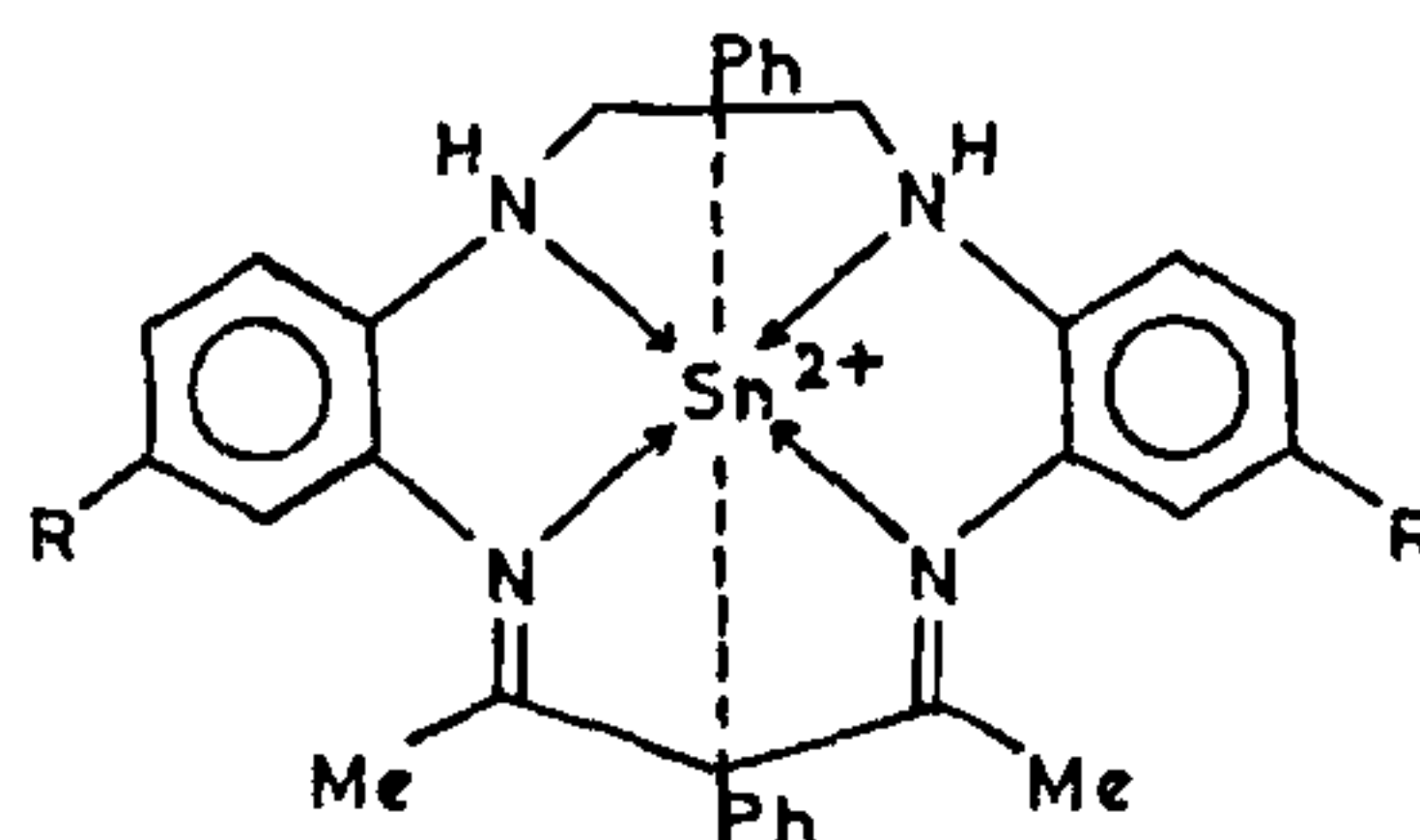
The elemental analysis data (table 1) indicate 1:1 ligand:tin stoichiometry for the complexes while the conductance data suggest these to be 1:2 electrolytes. Hence they could be formulated as  $[\phi_2\text{SnL}]X_2$  where  $\text{L} = \text{L}_1, \text{L}_2$  or  $\text{L}_3$  and  $\text{X} = \text{ClO}_4^-, \text{BF}_4^-$ .

In the IR spectra of the complexes of ligand  $\text{L}_1$ , the  $\nu_{\text{NH}}$  band<sup>8,9</sup> appears at  $3310\text{ cm}^{-1}$  and nitro group vibrations are seen at  $1510\text{ cm}^{-1}$  and  $1340\text{ cm}^{-1}$ , which correspond to the vibrations of the co-ordinated groups<sup>10,11</sup>. In the complexes of ligands  $\text{L}_2$  and  $\text{L}_3$  the latter vibrations disappear and  $\nu_{\text{NH}}$  and azomethine stretches appear at  $3300$  and  $1630\text{ cm}^{-1}$  respectively, the negative shift suggesting their co-ordination<sup>12</sup>. The bands at  $620\text{--}640\text{ cm}^{-1}$  and  $1040\text{--}1070\text{ cm}^{-1}$  in the perchlorate complexes and the bands at  $520\text{--}530\text{ cm}^{-1}$  and  $1010\text{--}1030\text{ cm}^{-1}$  in tetrafluoroborate complexes correspond to ionic groups<sup>13</sup> and confirm the conductivity values. A single weak band at  $290 \pm 10\text{ cm}^{-1}$  in the spectra of all the complexes is assigned to  $\nu_{\text{sym. Sn-C}}$  stretching mode indicating the presence of phenyl groups attached to tin<sup>14,15</sup>.

On the basis of the above data the following structures are suggested for the complexes.



Complex with  $\text{L}_1$  and  $\text{L}_2$   
( $\text{R} = \text{NO}_2$  for  $\text{L}_1$ ,  $\text{NH}_2$  for  $\text{L}_2$ )



Complex with  $\text{L}_3$   
( $\text{R} = \text{NH}_2$ )

4 June 1988; Revised 17 September 1988

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### DISCOVERY OF A TEPHRA BED IN THE QUATERNARY ALLUVIAL SEDIMENTS OF PUNE DISTRICT (MAHARASHTRA), PENINSULAR INDIA

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A vitric rhyolite tephra bed has been discovered in the Quaternary alluvial deposits exposed in the Kukdi river section near Bori village, district Pune,

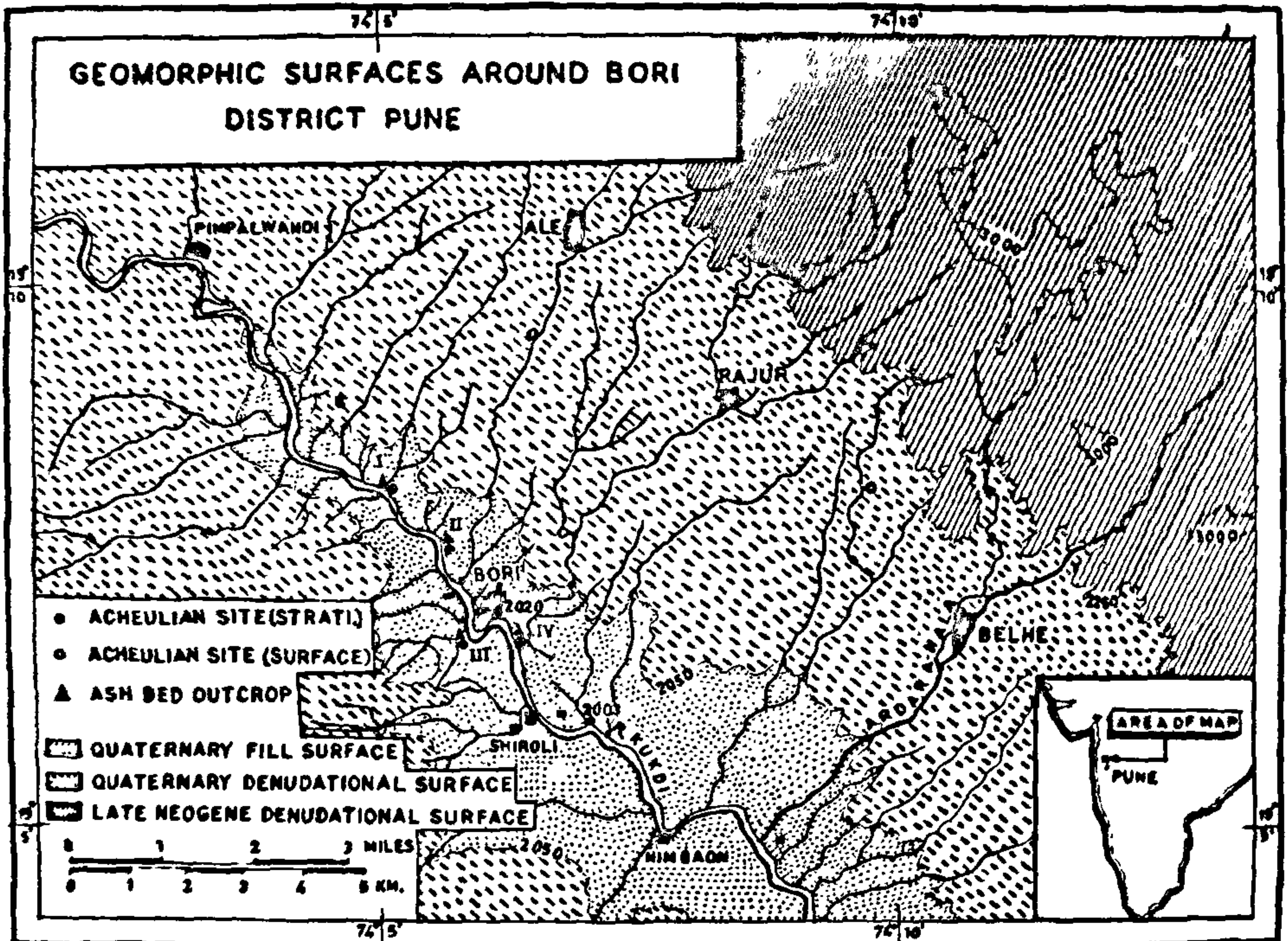


Figure 1. Location map of the study area. Sample locations are indicated as I, II, III and IV.