

of the internal modes of  $\text{WO}_6$ , one can distinguish the weak bands due to the water molecule. Assignment of bands due to external modes is difficult in a powder spectrum.

One of the authors (DP) is thankful to CSIR, New Delhi, for a fellowship.

12 September 1988

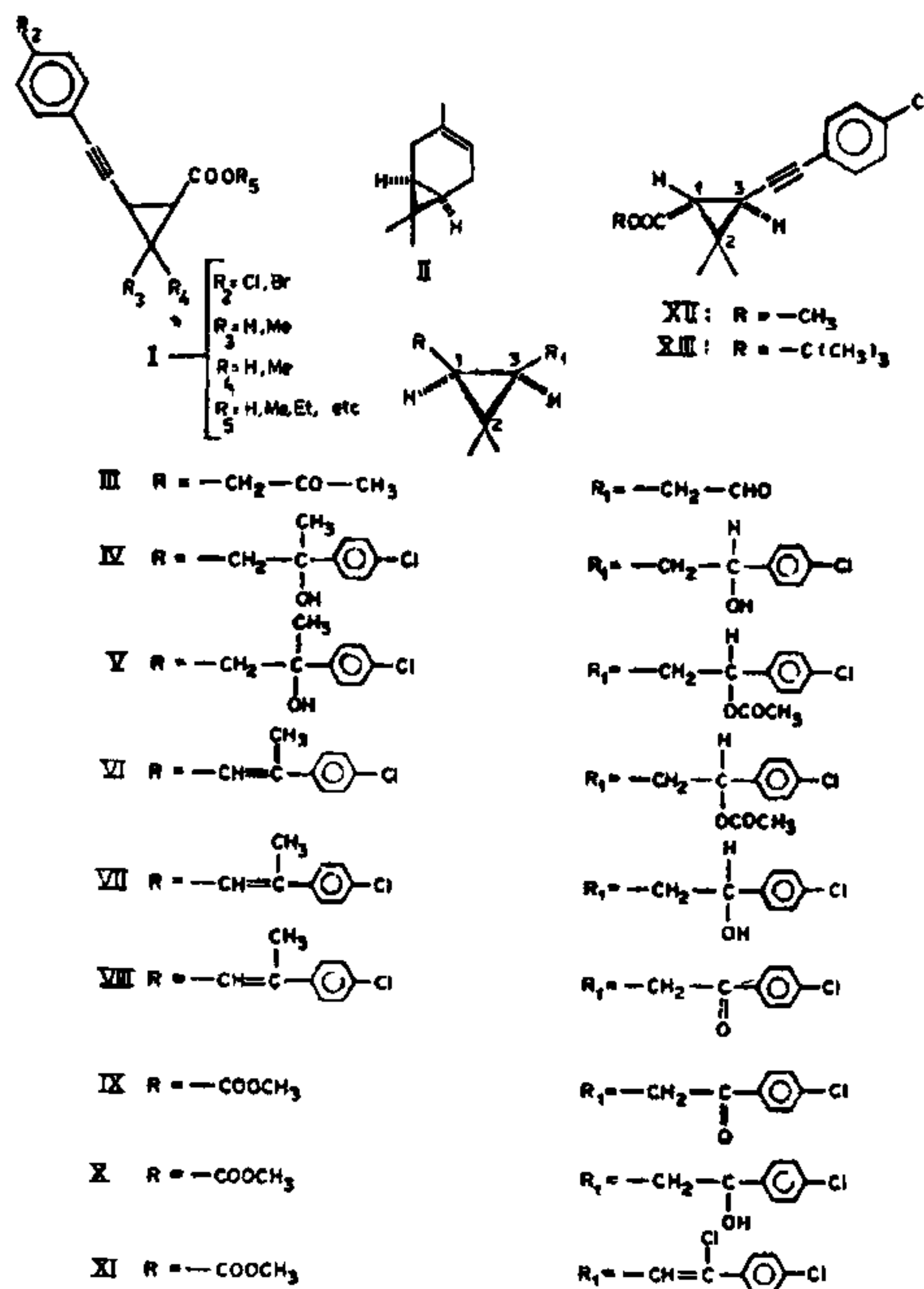
1. Szymanski, J. T. and Roberts, A. C., *Can. Mineral.*, 1984, 22, 681.
2. Miller, P. J., *Spectrochim. Acta*, 1970, A22, 957.
3. Legeois-Duyckaerts, G. and Tarte, P., *Spectrochim. Acta*, 1974, A30, 1771.
4. Blasse, G. and Corsmit, A. F., *J. Solid State Chem.*, 1973, 6, 513.
5. Vinogradov, S. N. and Linnel, R. H., *Hydrogen bonding*, Van Nostrand, New York, 1970.

### STEREOSPECIFIC SYNTHESIS OF METHYL/*t*-BUTYL (+)-1*R*-*TRANS*-2, 2-DIMETHYL-3-(2-*p*-CHLOROPHENYLETHYNYL)CYCLOPROPANECARBOXYLATES FROM (+)-3-CARENE

S. S. BHOSALE and G. H. KULKARNI  
National Chemical Laboratory, Pune 411 008, India.

IN an earlier communication<sup>1</sup>, we reported the synthesis of 3-phenoxybenzyl (+)-1*R*-*trans*-2, 2-dimethyl-3-(2-*p*-chlorophenyl-2-chlorovinyl/2-*E*-*p*-chlorostyryl/2-*p*-chlorophenylethynyl)cyclopropanecarboxylates. Some of these esters have been already reported to possess insecticidal, acaricidal and ectoparasiticidal activities. Kishida *et al*<sup>2</sup> have synthesized substituted 2-ethynylcyclopropane-1-carboxylic acid esters of type I, patented for their insecticidal, herbicidal, anti-inflammatory properties and also as hypoglycemic agents. In this communication, we report an alternative stereospecific route for the optically active esters of type I, viz. XII and XIII from (+)-3-carene (II).

Grignard reaction on ketoaldehyde (III), obtained from (+)-3-carene (II), using *p*-chlorophenylmagnesium bromide (2.5 mol), gave a diastereomeric mixture of diols (IV, 72%),  $\text{C}_{22}\text{H}_{26}\text{O}_2\text{Cl}_2$ , as a thick liquid identified by spectral data. IR<sup>\*\*</sup>: 3380 (OH), 1598 (aromatic). PMR ( $\text{CDCl}_3$ ): 0.44 (2H, *m*,  $\text{C}_1$  and  $\text{C}_3$  H), 0.64, 0.70, 0.80, 0.88, 0.96, 1.04 (6H, *s* each, cyclopropanemethyls of diastereomers), 1.56



(7H, *s* overlapping a multiplet,  $\text{CH}_2$  at  $\text{C}_1$  and  $\text{C}_3$  and tertiary methyl), 2.64 (2H, *s*, exchangeable with  $\text{D}_2\text{O}$ , hydroxy H), 4.72 (1H, *m*, benzylic H) and 7.36, 7.45 (8H, *s* each, aromatic H).

The hydroxymonoacetate (V) prepared from IV, afforded, on dehydration (pTSA/benzene), unsaturated acetate (VI, 90%) as a mixture of diastereomers,  $\text{C}_{24}\text{H}_{26}\text{O}_2\text{Cl}_2$ . IR: 1735, 1232 (acetate), 1598 (aromatic), 820 ( $-\text{CH}=\text{C}-$ ). PMR ( $\text{CDCl}_3$ ): 0.68 (1H, *m*,  $\text{C}_3$  H), 0.84, 1.00, 1.06, 1.14 (6H, *s* each, cyclopropanemethyls of diastereomers), 1.32 (1H, *m*,  $\text{C}_1$  H), 1.8 (2H, *m*,  $\text{CH}_2$  at  $\text{C}_3$ ), 2.04 (6H, *brs*, vinyl and acetate methyls), 5.35–5.74 (2H, *brm*, olefinic and benzylic H of diastereomeric *E* and *Z* isomers) and 7.28, 7.36 (8H, *s* each, aromatic H).

The corresponding unsaturated alcohol (VII) obtained from VI by saponification (KOH, MeOH) gave, on Jones oxidation, the expected ketone (VIII, 76%),  $\text{C}_{22}\text{H}_{22}\text{OCl}_2$ .  $[\alpha]_D^{25} + 19.5^\circ$  (*c*, 0.5,  $\text{CHCl}_3$ ).

\*Satisfactory elemental analysis has been obtained for all the compounds reported.

\*\*IR bands expressed in  $\nu$  ( $\text{cm}^{-1}$ ) and PMR chemical shifts in  $\delta$  (ppm) with TMS as internal standard.

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.

*Indian J. Chem.*, 1985, B24, 543.

- Kishida, Y., Masafumi, Y. and Noburu, I., *Ger Offen.*, 21 32761, 20 Jan. 1972, Sankyo Co. Ltd.; *Chem. Abstr.*, 1972, 76, 99205z.
- Newman, M., Parenkel, G. and Kirn, W., *J. Org. Chem.*, 1963, 28, 1851.
- Kondo, K., Matsui, K. and Takahatake, *Tetrahedron Lett.*, 1976, 4359.
- Matsui, M., Yoshioka, H., Yamada, Y., Sakamoto, H. and Kitahara, T., *Agric. Biol. Chem.*, 1965, 29, 784.

## CO-ORDINATION COMPLEXES OF DIORGANOTIN

P. R. SHUKLA, MALVIKA BHATT and NIHAL AHMAD

*Chemistry Department, Lucknow University, Lucknow 226 007, India.*

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

- Bhosale, S. S., Kulkarni, G. H. and Mitra, R. B.,