

Preliminary communication

Reaction of *cis*- and *trans*-(2-phenylcyclopropyl)trimethyltin with bromine or *N*-bromosuccinimide

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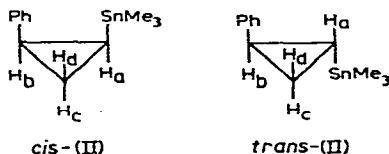
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For the halogenolysis of tetraalkyltin compounds Boue, Gielen, and Nasielski¹ proposed an S_E2 mechanism in polar solvents and an S_Ei mechanism in nonpolar solvents on the basis of kinetic studies. They also reported that the *cis* (or *trans*)-2-methylcyclopropyl carbon-tin bond was cleaved by halogen with almost complete retention (>95%) of configuration². By contrast, our study of the iodinolysis of optically-active (1-methyl-2,2-diphenylcyclopropyl)trimethyltin (I) gave the racemic 1-iodo-1-methyl-2,2-diphenylcyclopropane³. This result, which was confirmed on reinvestigation⁴, indicates a radical mechanism for the cleavage of the cyclopropyl carbon-tin bond in (I). Additional information on halogenolysis of cyclopropyl carbon-tin bonds is to be reported.

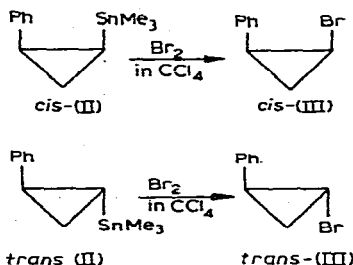
Treatment of *cis*- and *trans*-(2-phenylcyclopropyl)trimethyltin(II) with four equivalents of bromine in carbon tetrachloride solution at room temperature for 3 h in the dark under nitrogen atmosphere gave *cis*- and *trans*-1-bromo-2-phenylcyclopropane(III)^{5,6}★★, respectively, with complete retention (>98%) of configuration. This is consistent with

★Prepared by the reaction of trimethyltinlithium with *cis*- and *trans*-(III)⁵ with complete retention. Separation of *cis*- and *trans*-(II) was carried out by preparative gas chromatography. *cis*-(II): NMR(100 MHz, ppm downfield from TMS in CCl₄); 0.37 (m; H_a, J_{ab} 9.7 Hz, J_{ac} 10.4 Hz, J_{ad} 7.4 Hz), 2.27 (m; H_b, J_{bc} 8.0 Hz, J_{bd} 5.1 Hz), 1.15 (m; H_c, J_{cd} 4.3 Hz), 0.93 (m; H_d), 7.11 (d; phenyl protons), -0.22 (s, tin-methyl protons).



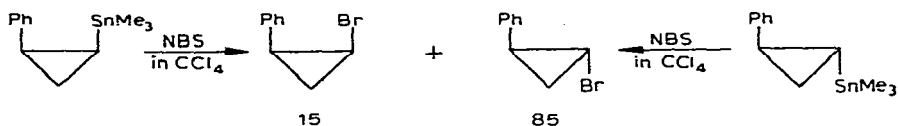
trans-(II): NMR; 0.23 (m; H_a, J_{ab} 6.3 Hz, J_{ac} 7.2 Hz, J_{ad} 10.0 Hz), 1.76 (m; H_b, J_{bc} 7.6 Hz, J_{bd} 4.6 Hz), 0.88 (m; H_c, J_{cd} 4.3 Hz), 1.03 (m; H_d), 6.98 (m; phenyl protons), 0.09 (s; tin-methyl protons).

★★Both geometrical isomers were determined by comparison of NMR spectra with the respective 1-chloro-2-phenylcyclopropane⁷.



the complete retention in the bromination of *cis*- and *trans*-(2-methylcyclopropyl)trimethyltin (IV)², and not with the racemization in the case of (I)^{3,4}. The cleavage of the cyclopropyl carbon-tin bond in (II) by bromine may thus involve an ionic mechanism.

Different behaviour is found under conditions of radical brominolysis. Davies, Roberts and Smith⁸ recently reported that *N*-bromosuccinimide (NBS) readily reacted with tetraalkyltin compounds by free radical chain mechanism. Bromination of (II) with NBS was carried out in carbon tetrachloride by heating to reflux for 4 h under nitrogen using α, α' -azobisisobutyronitrile as an initiator. A mixture of *cis*- and *trans*-(III) in the same ratio (15/85) was produced from both pure *cis*- and *trans*-(II). This is consistent with the specific formation of *trans*-1-iodo-2-phenylcyclopropane in iododecarboxylation of 2-phenylcyclopropanecarboxylate via a radical mechanism⁹.



The different behaviour of (I) from that of (II) or (IV) might be attributed to the difference between tertiary and secondary carbon-tin bonds. Further investigation of this point is in progress.

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