

Configurational Stability of Asymmetrically Substituted Organotin Compounds. An Example of Optical Activity at the Tin Centre

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Chemical shift non-equivalence of diastereotopic groups has been studied for a series of organotin monohalides with organic groups of different sizes to test the stereochemical stability of the asymmetric tin centre. The mutually related effects of halogen intermolecular exchange, nature of tin-halogen bond, intrinsic asymmetry of the molecules, and the steric requirements of the organotin groups are discussed in the light of the experimental findings. The effect of the bulk of the organic groups on the intrinsic asymmetry of some organotin compounds with four carbon-tin bonds has also been studied. An optically active tetraorganotin compound has been obtained through asymmetric synthesis.

ORGANOTIN chlorides undergo rapid inversion of configuration at the asymmetric organotin centre due to halogen-halogen exchange.^{1,2} This implies that this class of compounds does not have sufficient stereochemical stability to allow resolution and to be of use in determining the stereochemistry of substitution at tin. Conversely, an asymmetric organotin centre with four carbon-tin bonds shows a high stereochemical stability and could be optically resolved.¹ These studies were based^{1,2} on the chemical shift non-equivalence of diastereotopic nuclei.³ The ready halogen-halogen exchange⁴ in organotin halides seems to be at the origin of the phenomena observed and could involve an intermediate where the halogen atom links two or more molecules.² Addition of a good ligand^{1,5} such as acetone or dimethyl sulphoxide (DMSO) also gives rise to coalescence of diastereotopic protons. In this case, inversion can be explained on the basis of the formation of intermediate co-ordinate complexes of organotin halides since co-ordination of alkyltin halides with DMSO is a well established phenomenon.⁶⁻⁸ Organotin monohalides seem to give only 1:1 pentaco-ordinate complexes,⁸ with a trigonal bipyramidal structure. Even if these complexes, once formed, do not give any intermolecular halogen exchange, a non-dissociative, intramolecular exchange of ligands (*e.g.* pseudorotation) could cause a rapid redistribution between the sites of diastereotopic groups.

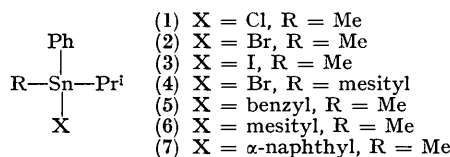
We report here some ¹H n.m.r. results relative to a number of asymmetric organotin halides which were selected for the purpose of analysing the effect of the size of the organic group and the nature of halogen on the halogen exchange process and on configurational inversion at the organometallic centre, both as a function of concentration in benzene or carbon tetrachloride solution and in the presence of a ligand such as methyl phenyl sulphoxide (PMSO).

A reaction leading from an asymmetric organotin halide to an optically active tetraorganotin compound was also preliminarily studied to check the possibility

of employing the asymmetric synthesis to elucidate the mechanism of substitution at the tin atom.

RESULTS AND DISCUSSION

The derivatives (1)–(7) were examined to compare the role of a different halogen atom on the intermolecular



halogen exchange process and consequently on the configurational stability of tin.

TABLE I

¹H N.m.r. parameters of compounds (1)–(3) in CCl₄ solution (0.3M) [δ (p.p.m.) from Me₄Si; J /Hz]

Compd.	$\delta(\text{CH}_{3\alpha})$	$\delta(\text{CH}_{3\beta})$	$J(^{117}/^{119}\text{Sn}-\text{C}-\text{H}_{\alpha})$	$J(^{117}/^{119}\text{Sn}-\text{C}-\text{H}_{\beta})$
(1)	0.71	1.39	49.8/53.0	96.3/101.2
(2)	0.79	1.38	49.9/52.7	98.1/102.4
(3)	0.93	1.36	51.6/54.0	99.7/103.7

Table I presents the more significant n.m.r. resonances of compounds (1)–(3). In CCl₄ and CS₂ solution these compounds do not show magnetic non-equivalence for the diastereotopic methyl groups. They were investigated in both solvents for a wide range of concentration and in CS₂ at temperatures down to -100 °C, but the methyl groups did not show separate signals within the limits of resolution of our n.m.r. instrument (0.3 Hz). At temperatures lower than -60 °C all the bands of the spectra tend to become slightly broad, the reference signal (Me₄Si) included, and this is probably due to an increase of viscosity of the solution.

The absence of non-equivalence may be due to the ready halogen-halogen exchange^{1,2} in these compounds in the solvents employed, but also a low intrinsic asymmetry could be responsible for the fact that non-equivalence is not observed in any one of the experimental

⁴ E. V. Van der Berghe, G. P. Van der Kelen, and Z. Eechaut, *Bull. Soc. chim. belges*, 1967, **76**, 79.

⁵ G. J. D. Peddle and G. Redl, *Chem. Comm.*, 1968, 626.

⁶ H. G. Langer and H. A. Blut, *J. Organometallic Chem.*, 1966, **5**, 288.

⁷ W. Kitching, *Tetrahedron Letters*, 1966, 3689.

⁸ W. Kitching, C. J. Moore, and D. Doddrell, *Austral. J. Chem.*, 1969, **22**, 1149.

¹ G. J. D. Peddle and G. Redl, *J. Amer. Chem. Soc.*, 1970, **92**, 365.

² D. V. Stynes and A. L. Allred, *J. Amer. Chem. Soc.*, 1971, **93**, 2666.

³ K. Mislow and M. Raban, in 'Topics in Stereochemistry,' eds. N. L. Allinger and E. Eliel, Interscience, New York, 1967, vol. 1, pp. 1–38.

conditions described above. In dilute benzene solution non-equivalence is observed even if restricted to a few hundredths of a part per million, as shown in Table 2.

TABLE 2

Values of $\Delta(A - B)$, the chemical shift [δ (p.p.m.)] difference between diastereotopic methyl groups for compounds (1)–(3) in different solvents

Compound	C_6H_6			
	$CCl_4(0.3M)$	$CS_2(0.3M)$	(0.3M)	(0.15M)
(1)	0.0	0.0	0.02	0.03
(2)	0.0	0.0	0.01	0.03
(3)	0.0	0.0	0.0	0.03

Coalescence is observed in more concentrated solution when the halogen is chloride, which should be connected * with a more difficult halogen–halogen exchange in the order $Cl > Br > I$. In chlorine derivatives, where the difference in electronegativity between tin and the halogen is higher than in the other cases, the synergic process of strengthening the tin–halogen bond through (*d-p*) π interactions should be more efficient,^{9,10} with more difficult halogen–halogen exchange as a result. In fluorine derivatives it is in fact easy to have a polymeric structure where fluorine is bonded to more than one tin atom.¹¹

In an attempt to slow down the rate of inversion of the asymmetric centre, bulky groups were attached to tin. In compound (4) where a methyl group has been replaced with a mesityl group the diastereotopic methyl groups of the isopropyl group are magnetically non-equivalent even in CCl_4 solution, as shown in Table 3.

TABLE 3

1H N.m.r. parameters for compound (4) in CCl_4 solution at room temperature and in tetrachloroethylene at different temperatures [δ (p.p.m.) from Me_4Si ; J/Hz]

	$CCl_4, 26^\circ$	$C_2Cl_4, 26^\circ$	50°	80°	120°
$\delta(CH_3)^a$	1.42	1.41	1.41	1.40	1.41
$\Delta(A - B)$	0.06	0.12	0.04	0.04	0.03
$J(^{117}/^{119}Sn-C-H)$	101.2/105.5				

^a Centre of the multiplet. ^b No significant changes as a function of temperature were observed.

Furthermore, non-equivalence is maintained even at temperatures above $100^\circ C$. Both an increase of intrinsic asymmetry and a slower rate of inversion in this compound could be responsible for this finding. In benzene solution coalescence is observed when the concentration of the compound is *ca.* 2M, but sharp lines are observed for concentrations up to 1M, while for 2,2-dimethylphenethyl(methyl)phenyltin chloride¹ peak broadening starts at a concentration of *ca.* 0.2M. Since, apparently, in the case of compound (4) halogen exchange takes place in more concentrated solution, this could indicate that this process is now more difficult. In any event it seems that the increased bulk of the organic group and of the halogen atom do not give a sufficiently high

* This is true if the diastereotopic peak separations for compounds (1)–(3) would be the same in absence of intramolecular halogen exchange which seems reasonable to assume from the data of Table 2, last column.

energy barrier to prevent inversion of configuration at the tin atom of organotin halides in concentrated solutions even of non-polar solvents. The results reported above are not, however, a clear indication of the increased amount of intrinsic asymmetry due to the bulk of the organic group since the halogen exchange and, possibly, conformational effects contribute to the observed chemical shift non-equivalence.

To clarify this point better, compounds (5)–(7) were analysed comparatively and it was found that the bulk of the organic group is in fact related to the size of the chemical shift non-equivalence. Compound (5) does not show non-equivalent diastereotopic groups

TABLE 4

1H Chemical shifts [δ (p.p.m.) from Me_4Si] for compound (4) in benzene solution at different concentrations

$[C_6H_6]/M$	0.08	0.17	0.68	1.0	1.35	2.0 ^b
$\delta(CH_3)^a$	1.38	1.38	1.38	1.37	1.38	1.4
$\Delta(A - B)$	0.11	0.10	0.09	0.08	0.06	<i>ca.</i> 0

^a Centre of the multiplet. ^b The spectrum shows broad peaks.

either for the methyls of the isopropyl group or for the benzylic protons: this was verified for CCl_4 at room temperature and for CS_2 down to $-100^\circ C$. For compounds (6) and (7) non-equivalence appears for CCl_4 solution at room temperature, while no change in $\Delta(A - B)$, the difference in chemical shift between non-equivalent methyl groups, is observed as a function of temperature. This fact also indicates that conformational equilibria are not a major cause of the size of the magnetic non-equivalence observed. Some n.m.r. parameters for these compounds are reported in Table 5.

TABLE 5

1H N.m.r. parameters for compounds (5)–(7) in CCl_4 solution (*ca.* 0.3M) [δ (p.p.m.) from Me_4Si ; J/Hz]

Compound	(5)	(6)	(7)
$\delta(CH_{3\alpha})$	0.10	0.51	0.56
$\delta(CH_{3\beta})$	1.20	1.32	1.34
$\Delta(A - B)$	0.0	0.04	0.05
$J(^{117}/^{119}Sn-C-H_\alpha)$	49.1/51.6	46.6/49.1	48.0/50.6

The bulk of the organic group and the nature of the tin–halogen bond should also be important in the formation of tin co-ordinate complexes. Employing derivative (4) and adding PMSO we observe that coalescence of the methyls of the isopropyl group in benzene solution is obtained for an organotin compound:PMSO ratio which is not too different from that necessary for the compound employed by Peddle and Redl¹ in the presence of DMSO. It seems from these data that the tin atom is too large for these phenomena to be markedly affected by increased bulk of organic groups. From the i.r. spectra¹² of the mixture of compound (4) and PMSO

⁹ J. E. Bissey, *J. Chem. Educ.*, 1967, **44**, 95.

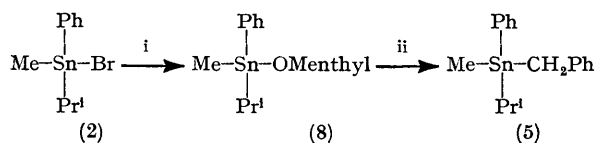
¹⁰ G. Barbieri and F. Taddei, *J.C.S. Perkin II*, 1972, 1327.

¹¹ H. C. Clark, R. J. O'Brien, and J. Trotter, *Proc. Chem. Soc.*, 1963, 85; H. C. Clark, R. J. O'Brien, and J. Trotter, *J. Chem. Soc.*, 1964, 2332.

¹² U. Folli and F. Taddei, unpublished results.

in the ratio 15:1 we observe that a large amount of sulphoxide is not associated ($\nu_{\text{SO(free)}}$ 1055, $\nu_{\text{SO(ass.)}}$ 995 cm^{-1}) and we believe that the complex with sulphoxide in dilute benzene solution is in rather low concentration. The sulphoxide should thus act on configurational stability through a complexation mechanism,^{1,2} but it should also exert a marked effect on halogen exchange by increasing the polarity of the solution. It is known in fact that coalescence is easier to obtain in polar solvents.^{1,5}

As pointed out previously,¹ it should be possible to resolve optically active organotin compounds with four carbon-tin bonds, since they seem to have a high stereochemical stability. In any event, we believe that their importance in investigating the stereochemistry of substitution at tin might be more important than is generally thought,¹ if this optical activity is obtained through a reaction which enables one to investigate the stability of the asymmetric tin atom. To this end we performed the reactions of the Scheme which make

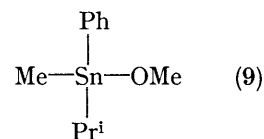


SCHEME Reagents: i, menthyl-OLi; ii, PhCH_2MgCl

use of (–)-menthol. In methanol solution compound (5) has $[\alpha]_{\text{D}} = +4.6^\circ$. If the reaction is repeated by substituting compound (2) with triphenyltin chloride, the final compound does not, as expected, show optical activity. This result implies that either step i or step ii leads to asymmetric synthesis and we formulate the following two hypotheses. (a) If this is true of step i, since a molar ratio 1:1 between (2) and menthyl-OLi has been used none of the two diastereomeric alkoxides (8) could prevail unless the enantiomeric organotin halide of (2) which is reacting faster [diastereomeric transition states are involved going from (2) to (8)] is not immediately regenerated through a rapid inversion at the tin centre [this implies for compound (2) a faster rate of inversion than of reaction]. The optical activity in the final compound (5) could then be considered to reflect the different ratio in which the two diastereomers (8) are formed during step i, assuming that no equilibration is taking place between them. (b) Alternatively, the decisive step could be ii if the two diastereomeric alkoxides (8) are rapidly equilibrating, so that a different ratio between them would arise because of their different thermodynamic stability. Since an excess of reagent was used in this step too, the optical activity in the final product (5) may reflect this different thermodynamic stability or be further modified through a rapid regeneration of that diastereomer which is reacting faster. At this stage we cannot give a definite answer to this problem, since several points in this reaction have to be cleared up.

¹³ M. Gielen, J. Nasielski, and J. Topart, *Rec. Trav. chim.*, 1968, **87**, 1051.

A preliminary check carried out on the asymmetric organotin compound (9) containing an alkoxy-group showed that the diastereotopic Me groups are aniso-



chronous in dilute benzene solution and collapse when the concentration is increased to *ca.* 1.8M. Furthermore, addition of methanol also causes collapse of compound (9) in dilute benzene solution. This shows that in this compound the inversion at tin, which is probably associated with intermolecular exchange of alkoxy-groups, is an easy, fast process, and this seems to support the second of our hypotheses on the asymmetric synthesis described. Attempts to study compound (8) directly have failed owing to the complexity of its n.m.r. spectrum. A more detailed investigation on the asymmetric synthesis of tetraorganotin compounds through diastereomeric organotin alkoxides is under progress.

EXPERIMENTAL

¹H N.m.r. spectra were obtained with a JEOL JNM-C-60HL spectrometer by employing solutions of the compounds freshly prepared.

Methyl(phenyl)isopropyltin Chloride (1).—A solution of dry HCl in absolute methanol (0.464N, 108 ml) was added dropwise (5 h) to a stirred solution of methyl(diphenyl)isopropyltin (16.55 g, b.p. 136° at 1.7 mmHg; n_{D}^{21} 1.5793 (lit.¹³ b.p. 118° at 0.15 mmHg; n_{D}^{20} 1.580), in absolute methanol (150 ml), cooled at -5° and protected from light and moisture. The solution was then allowed to reach room temperature slowly. The solvent, together with any volatile material, was evaporated and the residue was fractionally distilled under high vacuum. A first fraction (1.46 g) b.p. 72–76° at 0.06 mmHg, containing trace amounts of methylisopropyltin dichloride (n.m.r.) was discarded. The pure product (12.4 g, 86%) was then collected, b.p. 76–77° at 0.06 mmHg; $n_{\text{D}}^{23.5}$ 1.5602 (Found: C, 41.85; H, 5.0; Cl, 12.05; Sn, 40.85. $\text{C}_{10}\text{H}_{15}\text{ClSn}$ requires C, 41.5; H, 5.2; Cl, 12.25; Sn, 41.0%).

Methyl(phenyl)isopropyltin Bromide (2).—This was prepared according to a known procedure¹³ and had b.p. 102–103° at 0.2 mmHg; n_{D}^{22} 1.5770 (lit.¹³, b.p. 90–91.5° at 0.15 mmHg; n_{D}^{20} 1.578).

Methyl(phenyl)isopropyltin Iodide (3).—A solution of iodine (5.01 g) in absolute methanol was added dropwise (5 h) to a stirred solution of methyl(diphenyl)isopropyltin (5.62 g) in absolute methanol (70 ml), cooled to -5° , and protected from light and moisture. The procedure described for (1) was then followed. After discarding some head fractions, the pure compound (5.7 g; 75%) was collected by high vacuum fractionation, b.p. 94.5–95.5° at 0.05 mmHg; n_{D}^{22} 1.6082 (Found: C, 31.6; H, 3.95; I, 35.65; Sn, 30.95. $\text{C}_{10}\text{H}_{15}\text{ISn}$ requires C, 31.55; H, 3.95; I, 33.3; Sn, 31.15%).

Triphenylisopropyltin.—A solution of triphenyltin chloride¹⁴ (25.68 g) in anhydrous tetrahydrofuran (50 ml) was

¹⁴ H. Gilman and S. D. Rosemberg, *J. Amer. Chem. Soc.*, 1952, **74**, 5580.

added dropwise to a stirred Grignard reagent prepared under nitrogen in absolute ether (120 ml) from magnesium dust (3.24 g) and isopropyl bromide (16.4 g). The mixture was refluxed overnight and then carefully hydrolysed (external cooling) with a saturated aqueous solution of ammonium chloride. The organic layer was separated and the water layer was extracted with ether ($\times 3$). The organic solutions were then combined and dried (MgSO_4). After evaporation of the solvent, a white solid remained, which was crystallized from 95% ethanol, to yield product (25 g, 95%), m.p. 98–100°. The m.p. did not rise on further crystallization (Found: C, 64.46; H, 5.78. Calc. for $\text{C}_{21}\text{H}_{22}\text{Sn}$: C, 64.15; H, 5.65%). For this compound a different m.p. (84°) has been reported.¹⁵

Phenylisopropyltin Dibromide.—A solution of bromine (20.97 g) in absolute methanol (100 ml) was added dropwise (2 h) to a stirred suspension of triphenylisopropyltin (25.8 g) in absolute methanol (125 ml), cooled at -10° . A clear solution was obtained after about one-half of the bromine was consumed. When the addition was completed and the colour of free bromine disappeared, the solvent and bromobenzene co-product were evaporated and the residue fractionally distilled in vacuum, yielding product (23.4 g, 89.5%), b.p. 120° at 1.3 mmHg; n_D^{19} 1.6136 (Found: C, 27.8; H, 3.35; Br, 40.25; Sn, 28.85. $\text{C}_9\text{H}_{12}\text{Br}_2\text{Sn}$ requires C, 27.1; H, 3.05; Br, 40.1; Sn, 29.75%).

Mesityl(phenyl)isopropyltin Bromide (4).—A Grignard reagent was prepared under nitrogen by reaction of bromomesitylene¹⁶ (11.51 g) and magnesium dust (1.83 g) in anhydrous tetrahydrofuran (12 ml) following a reported procedure.¹⁷ The reagent was further diluted with anhydrous tetrahydrofuran (75 ml), filtered under nitrogen through a glass wool plug, collected in a dropping funnel and added dropwise (2 h) to a stirred solution of phenylisopropyltin dibromide (23.05 g) in anhydrous tetrahydrofuran (100 ml) cooled at -20° (owing to the bulk of the Grignard reagent a selective monosubstitution of the organotin dihalide was possible in this case; normally mono- and di-substitution, as well as no substitution occurs¹⁸). The mixture was allowed to reach room temperature slowly. Dry ether (200 ml) was added and the mixture treated dropwise with an aqueous saturated solution of ammonium bromide, cooling externally with an ice-salt bath (it is essential to use ammonium bromide in order to avoid hydrolysis of the organotin bromide). The organic layer was separated and dried (MgSO_4). The aqueous layer was further extracted with ether ($\times 3$), the ether solutions combined, the drying agent filtered off, and the solvent evaporated. The residue, under high vacuum fractionation, gave product (20.05 g, 75%), b.p. 143° at 0.02 mmHg; n_D^{22} 1.6150 (Found: C, 49.2; H, 5.2; Br, 18.55. $\text{C}_{18}\text{H}_{23}\text{BrSn}$ requires C, 49.35; H, 5.25; Br, 18.25%).

Benzyl(methyl)(phenyl)isopropyltin (5).—A solution of methylphenylisopropyltin bromide (2) (5.01 g) in absolute ether (20 ml) was added dropwise to a stirred Grignard reagent in absolute ether (43 ml) prepared under nitrogen from magnesium dust (0.73 g) and benzyl chloride (3.80 g). The mixture was refluxed overnight and then carefully hydrolysed (external cooling) by dropwise addition of an aqueous, saturated solution of ammonium chloride. The

organic layer was extracted with ether ($\times 3$). The combined organic solutions were dried (MgSO_4), the solvent evaporated, and the residue fractionally distilled under high vacuum to give product (4 g, 77.5%), b.p. 112° at 0.05 mmHg; n_D^{28} 1.5800 (Found: C, 59.55; H, 6.35. $\text{C}_{17}\text{H}_{22}\text{Sn}$ requires C, 59.15; H, 6.45%).

Mesityl(methyl)(phenyl)isopropyltin (6).—A Grignard reagent was prepared under nitrogen by reaction of bromomesitylene¹⁶ (5.79 g) in anhydrous tetrahydrofuran (6 ml) with magnesium dust (0.95 g),¹⁷ and further diluted with anhydrous tetrahydrofuran (30 ml). A solution of methyl(phenyl)isopropyltin bromide (2) (5.01 g) in anhydrous tetrahydrofuran (30 ml) was then added dropwise with stirring. The mixture was refluxed overnight, cooled, diluted with ether (100 ml), and then hydrolysed and worked-up as described for (5) to give product (3.8 g, 6.8%), b.p. 130 – 131° at 0.05 mmHg; $n_D^{27.5}$ 1.5730 (Found: C, 61.65; H, 7.0. $\text{C}_{19}\text{H}_{26}\text{Sn}$ requires C, 61.15; H, 7.0%).

Methyl-(α -naphthyl)(phenyl)isopropyltin (7).—A solution of methylphenylisopropyltin bromide (2) (5.01 g) was added dropwise to a stirred Grignard reagent, prepared under nitrogen in anhydrous tetrahydrofuran (33 ml) from magnesium dust (0.73 g) and α -bromonaphthalene¹⁹ (6.21 g). The mixture was refluxed overnight and then worked up as described for (5) to give product (34 g, 70%), b.p. 153 – 156° at 0.05 mmHg; n_D^{26} 1.6330 (Found: C, 63.2; H, 5.9. $\text{C}_{20}\text{H}_{23}\text{Sn}$ requires C, 63.05; H, 5.8%).

Asymmetric Synthesis of Compound (5).—All the steps of the reactions were carried out under nitrogen. A solution of n-butyl-lithium in ether was prepared from n-butyl bromide (1.37 g, 10 mmol) following a reported procedure.²⁰ The lithium reagent was filtered through a glass wool plug, collected in a dropping funnel, and added dropwise to a stirred solution of (–)-menthol (2.34 g, 15 mmol) in absolute ether (15 ml) at 0° . Stirring was continued for 30 min at room temperature. To the stirred mixture, again cooled at 0° was added dropwise a solution of methyl(phenyl)isopropyltin bromide (2) (3.34 g, 10 mmol) in absolute ether (20 ml). After stirring overnight at room temperature, the mixture was filtered through a glass wool plug and collected in a dropping funnel, then added dropwise to a stirred solution in ether (33 ml) at 0° of a Grignard reagent prepared from magnesium dust (0.97 g, 0.07 g atom) and benzyl chloride (5.06 g, 40 mmol). The mixture was stirred at room temperature overnight, and then hydrolysed with a saturated aqueous solution of ammonium chloride. The ether layer was separated and the aqueous layer was extracted with more ether ($\times 3$). The combined ether solutions were dried (MgSO_4). The solvent was evaporated in vacuum. The residue, consisting of optically active (5) and (–)-menthol, was separated into its components by means of preparative t.l.c. on silica gel containing a u.v. indicator.* The plates were developed twice with ligroin (b.p. 80 – 120°), and the separation of (5) and (–)-menthol was controlled by means of a Wood lamp. The upper part of the plate, containing (5), was extracted with ether. The ether was evaporated and the residue was identified as (5) by comparison of the n.m.r. and i.r. spectra with those of an authentic sample. The absence of (–)-menthol was also tested by g.l.c. analysis,

* Kieselgel DSF-O (Camag).

¹⁵ L. M. Snegur and Z. M. Manulkin, *Zhur. obshchei Khim.*, 1964, **34**, 4030 (*Chem. Abs.*, 1965, **62**, 9164).

¹⁸ L. I. Smith and F. H. McDougall, *J. Amer. Chem. Soc.*, 1929, **51**, 3002.

¹⁷ R. T. Hawkins, *J. Amer. Chem. Soc.*, 1953, **82**, 3053.

¹⁸ H. Gilman, *Chem. Rev.*, 1960, **60**, 459.

¹⁹ H. T. Clarke and M. R. Brethen, *Org. Synth.*, 1961, **1**, 121.

²⁰ R. G. Jones and H. Gilman, *Org. Reactions*, 1951, **6**, 339.

and confirmed by the sign of its optical rotation, which was as follows: $[\alpha]_{589}^{20} +4.6^\circ$; $[\alpha]_{578}^{20} +4.9^\circ$; $[\alpha]_{546}^{20} +5.5^\circ$; $[\alpha]_{436}^{20} +11.1^\circ$; $[\alpha]_{365}^{20} +22.2^\circ$ (MeOH, c 2.83 g per 100 ml; l 1 dm).† After short-path distillation at *ca.* 0.05 mmHg the product still showed $[\alpha]_{585}^{20} +2.5^\circ$; $[\alpha]_{365}^{20} +13.3^\circ$ (MeOH; c 3.97 g per 100 ml; l 1 dm). In order to further test the consistency of this asymmetric synthesis the sequence of reactions described was performed on triphenyltin chloride.¹⁴ Benzyltriphenyltin was obtained, m.p. 90–92° (lit.,²¹ 90–91°), which was optically inactive down to 365 nm.

Methoxy(methyl)(phenyl)isopropyltin (9).—A solution of sodium methoxide in methanol (15 ml) was prepared in a

† The optical rotations were measured on a Perkin-Elmer model 141 polarimeter, the accuracy of which is $\pm 0.002^\circ$ for angular rotations up to 1° .

dropping funnel from metallic sodium (0.46 g) under anhydrous conditions. This was added dropwise to a stirred solution of methyl(phenyl)isopropyltin bromide (2) (6.67 g) at room temperature. After reflux for 1 h, the solvent was distilled off. Dry chloroform was added and the precipitated sodium bromide was filtered under nitrogen. The solvent was evaporated and the residue fractionated to give *product* (3.7 g, 67%), b.p. 79–80° at 0.05 mmHg; n_D^{22} 1.5312 (Found: C, 46.35; H, 6.4. $C_{11}H_{18}OSn$ requires C, 46.35; H, 6.35%).

M.p.s and b.p.s were not corrected.

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²¹ H. Gilman and S. D. Rosemberg, *J. Amer. Chem. Soc.*, 1952, **74**, 531.