Tetrahedron Letters No.1, pp. 33-36, 1967. Pergamon Press Ltd.
Printed in Great Britain.

OPTICALLY ACTIVE ORGANOTIN COMPOUNDS I

PREPARATION AND REACTION OF (1-METHYL-2,2-DIPHENYLCYCLOPROPYL)TRIMETHYLTIN

Keiiti Sisido, Sinpei Kozima and Kôiti Takizawa
Department of Industrial Chemistry, Kyôto University, Kyôto, Japan

(Received 24 September 1966; in revised form 24 October 1966)

The optically active organotin compound hitherto described is d-methylethyl-n-propyltin iodide which contains a dissymmetric tin atom and has been resolved via the d-camphorsulphonate salt. Since, however, this salt was optically unstable, the value of $[\alpha]_D$ varied between 0° and +23°.[1] Kipping failed to isolate optically active organotin halides possessing aromatic groups from the salts.[2]

Walborsky et al. have succeeded to prepare optically active organolithium compound[3] and Grignard reagent[4] with an asymmetric cyclopropane carbon atom.[5,6,7]

A similar synthesis of an optically active organotin compound with an asymmetric carbon atom directly attached to tin was carried out from an optically active cyclopropyl bromide[5] and the cleavage reactions of the asymmetric carbon-tin bond by hydrochloric acid and iodine were studied in order to obtain informations about the reaction mechanisms.

When (+)-(S)-1-bromo-1-methyl-2,2-diphenylcyclopropane[5] (I), $[\alpha]_D^{19}$ +32°, was treated with a tetrahydrofuran solution of trimethyltinlithium[8] (II) at 0° for 15 hr. in a nitrogen atmosphere, two products were obtained. The one was (+)-(1-methyl-2,2-diphenylcyclopropyl)trimethyltin (III), $[\alpha]_D^{21}$ +11.6° (c 1.45, chloroform), n_D^{21} 1.5742, yield, 44.1%. Anal. Calcd. for $C_{19}H_{24}Sn$: C, 61.52; H, 6.52. Found: C, 61.38; H, 6.33. The other was (-)-(R)-1-methyl-2,2-diphenylcyclopropane[5] (IV), $[\alpha]_D^{21}$ -39.0° (c 1.12, chloroform), yield, 37%, which was identified by elemental analysis as well as infrared and n.m.r. spectra. The separation of I, III and IV was carried out by gas chromatography; helium gas flowing at 100 ml./min., a 75 cm. x 6 mm. o.d. stainless steel column packed with "Thermol-3" (Simazu Co. Ltd.), column bath at 170°, sample chamber at 325°. Retention time of I, III and IV was 10.5, 26.0 and 5.5 min., respectively.

Essentially the same reaction was carried out with (-)-(R)-1-bromo-1-methyl-2, 2-diphenylcyclopropane[5] (I), $[\alpha]_D^{19}$ -45. 2°. The experimental results are summarized in Table.

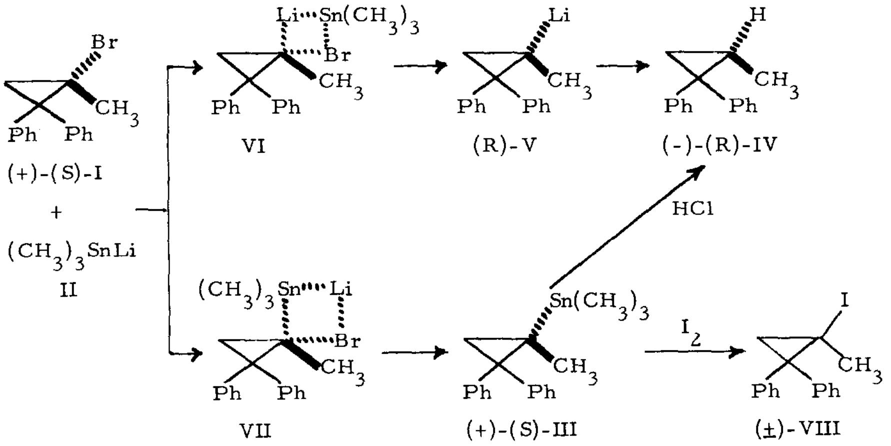
The 60 Mc. n. m. r. spectrum of III was analyzed as consisting of a phenyl multiplet (at 7. 04-7. 56 p. p. m.), four distinguishable methylene peaks (at 1. 09-1. 52 p. p. m.), a methyl singlet (at 1. 09 p. p. m.) and a sharp tin-methyl singlet (at -0. 22 p. p. m.) accompanied by small satellite peaks ($J_{117}Sn-CH_3$ = 50 c. p. s. , $J_{119}Sn-CH_3$ = 52 c. p. s.). Tetramethylsilane was used as an internal standard and deuterochloroform as a solvent. Infrared spectrum of III had the characteristic bands of phenyl group at 1603, 1495, 740 and 699 cm.$^{-1}$ and of methyl-tin group at 1180 and 760 cm.$^{-1}$

IV formed in this reaction had the same absolute configuration and optical purity as the starting material I. As to the possible route for the formation of IV, the reduction of I by trimethyltin hydride was proved not to be the case, since, when optically active (-)-(R)-I, $[\alpha]_D^{23}$ -96. 8° (optical purity: 86. 7%), was treated with an excess of trimethyltin hydride, which might be formed by the hydrolysis of II[8], greater part of I was recovered unchanged and optically inactive IV was obtained in a poor yield (5. 5%). This racemization indicated the free radical mechanism of the "tin hydride reduction," as reported by Kuivilla et al.[9]

Another possibility was that 1-methyl-2, 2-diphenylcyclopropyllithium[3] (V) might be an intermediate. Although an attempt was failed to confirm the existence of V by carbonation, the reaction of II with I might produce V involving a four-centered transition state (VI) as in the case of halogen-metal interchange reaction.[4] V should give IV with complete retention of the optical activity by solvolysis with tetrahydrofuran or by hydrolysis.[3] The fact that IV maintained its configuration as well as optical rotation would prove the case. III and II did not react to yield IV.

Treatment of (+)-III, $[\alpha]_D^{21}$ +11. 6°, with concentrated hydrochloric acid in carbon tetrachloride gave (-)-(R)-IV, $[\alpha]_D^{23}$ -39. 5° (c, 0. 53, chloroform), whose optical purity and configuration were just the same as those of the starting material I. This indicated that both formation reaction of tin-carbon bond from I and cleavage reaction of the bond by hydrochloric acid proceeded via ionic mechanism. From the fact that III was formed without change in the optical purity, the maximum rotation of III was calculated to be 39. 8°.

Since these cyclopropane derivatives have such a large barrier to inversion[3, 10] that complete inversion could not be considered to occur, this



TABLE

Preparation and Reaction of (1-Methyl-2, 2-diphenylcyclopropyl)trimethyltin

	I	III	IV[a]	IV[b]
$[\alpha]_D$	+32.5°	+11.6°	-39.0°	-39.5°
Optical purity[c]	29.1%		30.5%	30.9%
Weight (Yield)	0.93 g.	0.53 g. (44.1%)	0.25 g. (37.0%)	74.5%
$[\alpha]_D$	-45.2°	-16.1°	+51.3°	+53.1°
Optical purity	40.5%		40.1%	41.4%
Weight (Yield)	1.52 g.	1.21 g. (61.2%)	0.19 g. (17.2%)	81.4%

---

a) Produced by the reaction of I with II.

b) Produced by the reaction of III with concentrated HCl.

c) Maximum rotation of I and IV taken as 111.6° and 128°, respectively.[4]

tin-carbon bond formation would be proceeded via S_Ei reaction shown as VII similar to the formation reaction of IV via VI and V. From this it could be concluded that both the formation and the cleavage reactions of tin-carbon bond proceeded with complete retention, accordingly, the absolute configuration of III could be decided.

When (+)-III, $[\alpha]_D^{21}$ +11.6°, was treated with iodine in carbon tetrachloride, optically inactive iodide, (±)-1-iodo-1-methyl-2,2-diphenylcyclopropane (VIII) was obtained in 11.1% yield, m.p. 89° (lit.[3] m.p. 88° for the racemate, 119° for the enantiomer). Elemental analysis gave correct values. This racemisation showed that the cleavage reaction of tin-carbon bond by iodine proceeded via free radical mechanism. The S_N1 mechanism would not be considerable, since the cleavage by hydrochloric acid under the same condition proceeded by the ionic route with retention of the configuration.

Acknowledgment. We wish to thank Dr. Teturô Singû of the Faculty of Pharmaceutical Sciences, Kyôto University for the aid in obtaining the n.m.r. spectra.

REFERENCES

1) W. J. Pope and S. J. Peachey, Proc. Chem. Soc. 16, 42 (1900); ibid. 16, 116 (1900).
2) F. B. Kipping, J. Chem. Soc. 2365 (1928).
3) H. M. Walborsky, F. J. Impastato and A. E. Young, J. Am. Chem. Soc. 86, 3283 (1964).
4) H. M. Walborsky and A. E. Young, ibid. 86, 3288 (1964).
5) H. M. Walborsky and F. J. Impastato, ibid. 81, 5835 (1959).
6) H. M. Walborsky and F. M. Hornyak, ibid. 77, 6396 (1955); H. M. Walborsky and J. F. Pendleton, ibid. 82, 1405 (1960).
7) H. M. Walborsky, L. Barash, A. E. Young and F. J. Impastato, ibid. 83, 2517 (1961); H. M. Walborsky and C. G. Pitt, ibid. 84, 4831 (1962).
8) C. Tamborski, F. E. Ford and E. J. Soloski, J. Org. Chem. 28, 237 (1963).
9) H. G. Kuivila, L. W. Menapace and C. R. Warner, J. Am. Chem. Soc. 84, 3584 (1962).
10) F. J. Impastato and H. M. Walborsky, J. Am. Chem. Soc. 84, 4838 (1962).