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STEREOCHEMISTRY OF THE TIN–CARBON BOND

II *. BROMINOLYSIS OF A SERIES OF *exo*- AND *endo*-2-TRIORGANOSTANNYLNORBORNANES

ALAIN RAHM*, JACQUES GRIMEAU and MICHEL PEREYRE

Laboratoire de Chimie Organique du Silicium et de l'Etain, associé au CNRS (UA 35), Université de Bordeaux I, 351, cours de la Libération, 33405-Talence (France)

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Summary

The brominolysis of a series of *exo*- and *endo*-2-triorganostannylnorbornanes with methyl, isopropyl, neopentyl and cyclohexyl as substituents on tin, proceeds with inversion of configuration for the *endo*-carbon–tin bond and with retention of configuration for the *exo*-carbon–tin bond. The norbornyl system seems to favour the *exo*-approach of the electrophile.

In a previous study we reported stereochemical results for the brominolysis of a series of 2-triorganostannylbutanes [1]. We demonstrated that in a polar medium this electrophilic destannylation could, depending essentially on the steric hindrance at the tin center, follow a path resulting in retention of configuration. Recent work suggests that S_E2 reactions of tetraorganotin compounds are considerably more complex than earlier work indicated [2–6].

Following the synthesis of a series of fully characterized 2-triorganostannylnorbornanes [7], the stereochemistry of bromine cleavage of these stannanes was examined under various experimental conditions.

A. Brominolysis of *endo*-2-triorganostannylnorbornanes

Starting with isomerically pure 2-trialkylstannylnorbornane with alkyl = methyl, isopropyl, neopentyl and cyclohexyl [7], two sets of experiments were performed: one in methanol-cyclohexane as solvent (Exp. 1–4) and the other in chlorobenzene as solvent (Exp. 5–8). We confirmed that no isomerization of *endo*-2-bromonorbornane occurred during the bromine cleavage [7]. We believe that under the conditions

* For part I see Ref. 7.

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TABLE 1

STEREOCHEMISTRY OF BROMINOLYSIS OF *endo*-2-TRIALKYLSTANNYLNORBORNANES

Exp. no.	R	Conditions [a]	$C_7H_{11}Br/RBr$ [b,c]	$C_7H_{11}Br$ [b] *exo/endo*	Preferred stereochemistry (%)
1	Methyl	$MeOH/C_6H_{12}$ = 1/1 (dark)	< 1/ > 99 [d]	78/22	Inversion (78)
2	iso-Propyl	$MeOH/C_6H_{12}$ = 1/1 (dark)	60/40	68/32	Inversion (68)
3	neo-Pentyl	$MeOH/C_6H_{12}$ = 1/1 (dark)	55/45	73/27	Inversion (73)
4	cyclo-Hexyl	$MeOH/C_6H_{12}$ = 1/1 (dark)	56/44	74/26	Inversion (74)
5	Methyl	PhCl (dark)	< 1/ > 99 [d]	78/22	Inversion (78)
6	iso-Propyl	PhCl (dark)	78/22	65/35	Inversion (65)
7	neo-Pentyl	PhCl (dark)	66/34	68/32	Inversion (68)
8	cyclo-Hexyl	PhCl (dark)	59/41	65/35	Inversion (65)

[a] Initial concentration in stannane: 0.8 mol l^{-1}. Reaction time 18 h. Bromine addition was at −10°C and the reaction mixture was warmed to room temperature. [b] GLC analysis (see Experimental). [c] The R group to norbornyl ratio is 3/1 in the starting material. Experimental values have been corrected to take account of this statistical factor and results are given for a 1/1 R/norbornyl ratio. [d] No accurate measurements could be made with methyl bromide: methyl groups are cleaved off too readily and methyl bromide is too volatile.

used, radical contributions to the overall mechanism are insignificant because of the minor effect of hydroquinone. The results are presented in Table 1.

The alkyl groups were chosen because of their steric constants [8] (methyl, 0; isopropyl, 0.47; cyclohexyl, 0.79; neopentyl, 1.74) but increasing the front side steric bulk does not influence the stereoselectivity of brominolysis: from 65 to 78% inversion of configuration was observed. In an earlier work, Gielen and Nasielski demonstrated the influence of the polarity of the solvent on the mechanism of tin–carbon bond cleavage [9]. In our experiments almost no change of selectivity was observed on changing from the polar methanol cyclohexane mixture to the less polar chlorobenzene. This implies that there is no drastic change in mechanism. Moreover the regioselectivity of the bromine attack was not greatly modified by changing the polarity of the solvent, and the reactivity sequences are similar in both media, viz. methyl ≫ norbornyl > cyclohexyl > neopentyl > isopropyl. These observations are unexpected in relation to Gielen's findings on solvent effects [9].

In the case of 2-trimethylstannylnorbornane, although the methyl groups are cleaved much more readily, we were able to observe the formation of some 2-bromonorbornanes identified by GLC.

B. Bromolysis of *exo*-2-triorganostannylnorbornanes

A series of *exo*-2-trialkylstannylnorbornanes was prepared with alkyl = methyl, isopropyl, neopentyl and cyclohexyl [7]. As we were unable to obtain pure stereoisomers, experiments were performed with *exo*-derivatives containing 20% of the *endo*-isomer; 2-trimethylstannylnorbornane was used as pure *exo*-isomer. The results are summarized in Table 2.

It is obvious from Tables 1 and 2 that retention of configuration is the preferred stereochemistry in both polar (Exp. 9–12) and less polar (Exp. 13–16) media. The presence of hydroquinone (Exp. 17) did not significantly change the stereochemistry

TABLE 2

STEREOCHEMISTRY OF BROMINOLYSIS OF 2-TRIALKYLSTANNYLNORBORNANES IN 80% *exo*/20% *endo* MIXTURE

Exp. no.	R	Conditions [a]	$C_7H_{11}Br/RBr$ [b,c]	$C_7H_{11}Br$ [b] *exo/endo*	Preferred stereochemistry
9	Methyl [e]	$MeOH/C_6H_{12}$ = 1/1 (dark)	<1/>99 [d]	84/16	Retention
10	iso-Propyl	$MeOH/C_6H_{12}$ = 1/1 (dark)	65/35	68/32	Retention
11	neo-Pentyl	$MeOH/C_6H_{12}$ = 1/1 (dark)	51/49	72/28	Retention
12	cyclo-Hexyl	$MeOH/C_6H_{12}$ = 1/1 (dark)	52/48	64/36	Retention
13	Methyl [e]	C_6H_5Cl (dark)	<1/>99 [d]	83/17	Retention
14	iso-Propyl	C_6H_5Cl (dark)	80/20	64/34	Retention
15	neo-Pentyl	C_6H_5Cl (dark)	70/30	80/20	Retention
16	cyclo-Hexyl	C_6H_5Cl (dark)	65/35	80/20	Retention
17	cyclo-Hexyl	C_6H_5Cl/hydroquinone (dark)	67/33	78/22	Retention
18	cyclo-Hexyl	C_6H_5Cl (light)	60/40	55/45	Retention

[a] Initial concentration in stannanes: 0.8 mol l^{-1}. Reaction time 18 h. Bromine addition was at −10°C and the reaction mixture was warmed to room temperature. [b] GLC analysis (see Experimental). [c] See Table 1, note *c*. [d] See Table 1, note *d*. [e] Starting from pure *exo*-2-trimethylstannylnorbornane.

of the brominolysis, but a decrease of selectivity was observed when the reaction was carried out in the light (Exp. 18); the results confirm that radical contributions to the mechanism are insignificant under our experimental conditions.

The regioselectivity of the brominolysis is very close to that observed with the *endo*-isomers, and the reactivity sequence is also the same.

The stereochemical behaviour of 2-trialkylstannylnorbornanes in S_E2 reactions agrees closely with observations made by Kitching on *cis*- or *trans*-1-triisopropylstannyl-4-methylcyclohexane, which invariably gave *cis*-1-bromo-4-methylcyclohexane [5]. Our results are not explained by any of the models previously proposed for the brominolysis of the tin–carbon bond [2–6]. The observed selectivity is practically independent of the polarity of the reaction medium and of the bulk of the substituents. The competition between inversion and retention pathways seems to be dominated by the norbornyl system, which favours the *exo*-approach of the electrophile whatever the configuration of the starting material.

Experimental

The *exo*- and *endo*-2 trialkylstannylnorbornanes were synthesized as described in ref. 7.

Brominolysis of 2-trialkylstannylnorbornanes

A typical procedure was as follows. To a solution of 0.0043 mol of 2-trialkylstannylnorbornane in 1/1 MeOH/cyclohexane (3.8 cm^3) at −10°C was added 0.0043 mol of bromine in MeOH (5.2 cm^3). The stirred mixture was allowed to warm to room temperature and after 12 h the solvents were removed and the crude mixture was analyzed by GLC.

For brominolyses in PhCl, 3.8 and 5.2 cm^3 of solvent were used under the same conditions.

Yields of 2-bromonorbornane from *endo*-2-trialkylstannylnorbornanes, with yields from *exo*-2-trialkylstannylnorbornanes in parentheses, were as follows: (a) In MeOH/cyclohexane: methyl < 1% (< 1%), isopropyl 70% (87%), neopentyl 41% (67%), cyclohexyl 60% (84%). (b) In chlorobenzene: methyl < 1% (< 1%), isopropyl 72% (78%), neopentyl 45% (52%), cyclohexyl 63% (72%).

GLC analyses

GLC analyses were carried out on an Intersmat IGC 120 FB chromatograph equipped with a flame ionisation detector.

2-Bromonorbornanes were analyzed with a 1/8" × 15' column packed with 10% QF_1 on Chromosorb WAW DMCS 100–120 mesh; 1-bromooctane was used as internal standard and the 2-bromonorbornanes were identified by comparison with authentic samples [10].

Neopentyl bromide and cyclohexyl bromide were analyzed on the same column with cyclohexyl bromide and 1-bromooctane, respectively, as internal standards. Isopropyl bromide (with 1-bromopentane as internal standard) was analyzed on a 1/8" × 15' column packed with 10% Carbowax 400 on Chromosorb G AW DMCS 80–100 mesh.

Isomerization of the 2-trialkylstannylnorbornanes

Trimethyltin bromide was added to a solution of *endo*-2-triisopropylstannylnorbornane or of 80/20 *exo/endo* 2-triisopropylstannylnorbornane in 1/1 MeOH/cyclohexane. No isomerization was observed after 12 h. The 2-bromonorbornanes also underwent no isomerization under the same conditions.

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