OPTICALLY ACTIVE TRIARYLBORANES: SYNTHESIS AND STEREOISOMERIZATION OF ETHANO-BRIDGED TRIARYLBORANES

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Abstract: Ethano-bridged triarylboranes 1a-c were synthesized. The boranes 1b and 1c were resolved into optically pure form (the first example of optical resolution of triarylboranes). The activation parameters of the racemization were determined.

In relation to conformations and conformational isomerizations of triarylcarbenium ions,¹ isoelectronic triarylboranes have received considerable interest. Several triarylboranes which have relatively bulky substituents on the aryl groups have been investigated in terms of dynamic NMR by Mislow and his co-workers.² They showed the stereo-isomerizations of these propeller type of compounds proceed via two-ring flip mechanism with barrier of 14-18 kcal/mol. Optical resolution of triarylboranes at ambient or higher temperature has not been hitherto reported. Ethano-bridgings of aryl groups in triarylboranes should increase the activation energy of racemization. We report the first demonstration of optical resolution of triarylboranes at room temperature with utilizing the ethano-bridging technique.

Ethano-bridged triarylboranes (1a, 1b, and 1c) were synthesized via 1-bromo-2,6-bis[2-(2-bromoaryl)ethyl]benzene (5a, 5b, and 5c) according to Scheme I. Treatment of 1-bromo-2,6-(bromomethyl)benzene (2) with α -sulfonyl carbanion³ generated in DMSO gave a diastereomeric mixture (ca. 1 : 1) of bis-sulfone (4) in 74-99% yields. Reductive desulfonylation⁴ of 4 with Na-Hg in a mixed solvent (ethyl acctate-methanol, ca. 2 : 1 v/v) in the presence of an excess amount of bromobenzene (for 4a and 4b) or 1-bromonaphthalene (for 4c) gave tribromide 5 (5a in 70%, 5b in 77%, and 5c in 48% yields). Tri-lithiation of 5 with t-butyl lithium (ca. 6.3 eq) in ether at -30°C, followed by treatment with boron trifluoride etherate produced the desired ethano-bridged triarylboranes 1 (1a in 17%, 1b in 42%, and 1c in 39% yields).⁵ The boranes 1b and 1c are stable toward moisture and air, whereas 1a is rather moisture sensitive.⁶

¹H-NMR spectra of these boranes indicate that the molecules have fixed conformation in C_2 -symmetry in solution.⁵ In order to obtain



a: X=Y=H, b: X=Me, Y=H, c: X,Y= -HC=CH-CH=CH-



Figure 1. ORTEP view of 1b. Thermal ellipsoids are drawn at the 50% probability level.

easily resolved into optically pure form by preparative HPLC with use of a column packed with chiral stationary phase (CHIRALCEL OJ) 9 . Figure 2 shows CD- and UV-spectra of the resolved 1b and 1c. Rather complicated

definitive insight into the conformations of these triarylboranes, an X-ray structural analysis was undertaken for 1b.⁷ Τwο independent molecules having very similar structures were observed in a crystal One of these lattice. structures is shown in Figure 1. The analysis shows that the molecules almost lie on a C₂ axis (not crystallographic one). The boron and three carbon atoms bound to it are very nearly coplanar. The angle of rotation out of this plane is about 64.6° for the aromatic ring on the C₂ axis. The other two rings rotate out of this plane $46.3-47.4^{\circ}$ in the same direction, but in the different direction from the ring on the C₂ axis. The distance between the two methyl groups is about 3.9 Å.

The activation parameters of the racemization of borane 1a were determined to be $\Delta H^{\neq} = 16.3\pm0.5$ kcal/mol and $\Delta S^{\neq} = -1.5\pm0.5$ e.u by the analysis of temperaturedependent NMR spectrum of a complex ABCD pattern of ethano protons.⁸ The boranes 1b and 1c were



Figure 2. CD and UV spectra of (+)- and (-)-1b and 1c in hexane

patterns of Cotton effects indicate the interaction of chromophores through empty orbital of the boron. These optically pure boranes are stable at room temperature and racemize only at higher temperature (k = ca 1.0 x 10^{-5} s⁻¹ at 160°C for 1b, at 100°C for 1c). The activation parameters of this process were determined to be ΔH^{\neq} = 33.8±1.7 kcal/mol, ΔS^{\neq} = -4.1±0.4 e.u. for 1b, ΔH^{\neq} = 26.1±0.5 kcal/mol, ΔS^{\neq} = -12.2±0.4 e.u. for 1c by monitoring the racemization with the HPLC. Increase of activation enthalpy in the order of 1a→1c→1b will be attributed to the order of steric interference between the substituents of Xs (H→sp²C→sp³C) during the racemization. The considerably negative activation entropy of 1c indicates higher order of arrangement of naphthyl groups in the transition state.

In summary, optical resolution of triarylboranes was exemplified for the first time by bridging the aromatic rings with ethano-groups. The detailed analysis of CD-spectra involving the determination of absolute stereochemistries of **1b** and **1c** is in progress.

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- 5 1a: mp 106-107°C, m/z 294 (M⁺) ¹H-NMR (bromobenzene-d₅, ethano-region determined by simulation) $\delta H_1 = 2.64$, $\delta H_2 = 2.95$, $\delta H_3 = 3.03$, $\delta H_4 = 3.14$, $J_{12} = -13.39$, $J_{13} = 1.48$, $J_{14} = 5.25$, $J_{23} = 12.30$, $J_{24} = 1.36$, $J_{34} = -16.97$, 1b: mp 166-168°C, m/z 322(M⁺), ¹H-NMR (CD₂Cl₂, ethano-region determined by simulation) $\delta H_1 = 2.94$, $\delta H_2 = 3.15$, $\delta H_3 = 3.13$, $\delta H_4 = 3.23$, $J_{12} = -15.74$, $J_{13} = 2.87$, $J_{14} = 8.30$, $J_{23} = 10.51$, $J_{24} = 2.56$, $J_{34} = -16.63$ Hz: K. Satake, <u>Kaqaku</u> 1984, 39 (No 9, supplement), 1.; 1c: mp 271-272°C, m/z 394 (M⁺), ¹H-NMR (CDCl₃, ethano-region observed) $\delta H_1 = 2.93$, $\delta H_2 = 3.26$, $\delta H_3 = 3.47$, $\delta H_4 = 3.68$, $J_{12} = 14.6$, $J_{13} = 3.0$, $J_{14} = 6.0$, $J_{23} = 12.6$, $J_{24} = 2.8$, $J_{34} = 18.3$.
- 6 The separation and purification of 1a was carried out using a preparative HPLC (LC908) with a column packed with a synthetic polymer (JAIGEL-1H; available from Japan Analytical Industries)
- 7 Crystal data for 1b: $C_{24}H_{23}B$, triclinic space group Pl (No. 2), a = 13.725(3) Å, b = 15.770(4) Å, c = 8.832(2) Å, α = 91.06(2), β = 100.67(2), γ = 70.88(2), V = 1773.2(8) Å³, Z = 4, $\rho_{calc.}$ = 1.21 gcm⁻¹; Rigaku AFC5R; Mo K_{α} radiation [$\lambda(K_{\alpha})$ = 0.71069 Å]; 3 °< 20< 55°; 6500 unique reflections, of which 2030 were treated as observed [F² > $3\sigma(F^2)$]; R = 0.047, R_W = 0.045. Structural data have been deposited with the Cambridge Crystallographic Data Centre.
- 8 Temperature-dependent NMR spectrum and the simulated spectra for 1a will be described in full paper.
- 9 Available from Daicel Chemical Industries, Japan.

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