Journal of Organometallic Chemistry, 448 (1993) C1–C2

JOM 23335PC

Preliminary Communication

New 1,3-diacyloxy-1,3-diethyldiboroxanes. Equilibrium of chelate ring formation

Andrzej Sporzyński

Department of Chemistry, Warsaw University of Technology (Politechnika), Noakowskiego 3, 00-664 Warsaw (Poland)

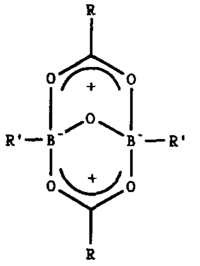
(Received October 13, 1992)

Abstract

New 1,3-diacyloxy-1,3-diethyldiboroxanes $[Et(RCOO)B]_2O$ containing electron-withdrawing atoms in the acyloxy group were synthesized. On the basis of ^{11}B NMR spectra the equilibrium between the forms containing tetra- and tricoordinated boron atoms is proposed. This equilibrium is influenced by the kind of acyloxy group and by the temperature.

1. Introduction

1,3-Diacyloxy-1,3-diorganodiboroxanes $[R'(RCOO)B]_2O$ are useful reagents in organic syntheses [1]. Preparation of the compounds with various R and R′ groups is described in the literature, starting from triorganoboranes [2–4], alkylchloroboranes [5,6], tetraorganodiboroxanes [7,8], organoboronic acids [9] or acyloxyorganoboron compounds [4,8]. The best methods for their synthesis are the reaction of tetraorganodiboroxanes with carboxylic acids [8] or the reaction of triorganoboroxins with carboxylic acid anhydrides [10], in which the desired compounds are formed quantitatively without by-products. The bicyclo[3.3.1] structure (**I**) proposed for these compounds [11] was



I

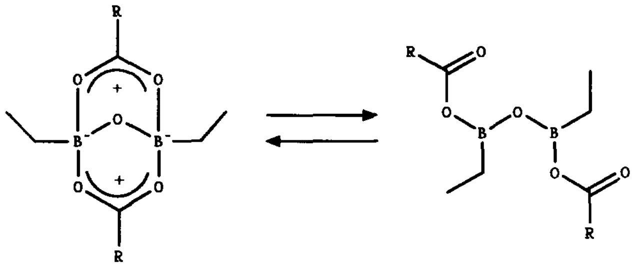
confirmed by ^{11}B and ^{17}O NMR spectroscopy for some diacyloxydiethyl compounds [10]. However, in the case of those compounds possessing an acyloxy group (an electron-withdrawing substituent) the spectral data show the presence of the form containing the tricoordinated boron atom. In this communication the characterization of some newly synthesized compounds is given.

2. Results and discussion

The investigated compounds were obtained by the reaction of triethylboroxin or tetraethyldiboroxane with the appropriate acid or anhydride (Scheme 1) and crystallized from heptane. Their yields, melting points and ^{11}B NMR data are collected in Table 1.

In ^{11}B NMR spectra only one signal is present for **1** at 9 ppm, which can be attributed to the tetracoordinated boron atom in **II**. For the compounds with mono- and dichlorosubstituted acetoxy group, **2** and **3**, a weak signal at 34.5 ppm is also present. The position of this signal corresponds to the tricoordinated boron atom. Introduction of further chlorine atoms causes the intensity of this signal to increase. Moreover, the position of the signal corresponding to the tetracoordinated boron atom shifts significantly to the left, indicating the weakening of the donor properties of oxygen atoms. The rise of the temperature also increases the intensity of the tricoordinated boron signal.

These facts can be explained by the equilibrium between two forms of diacycloxydiethyldiboroxanes — **II** with bicyclic chelate structure and **III** with tricoordinated boron atom:



II III

This equilibrium depends on the kind of acyloxy group present and on the temperature. For diacetyldiethyldiboroxane the equilibrium is completely shifted to the left, even with elevated temperatures [10]. Introduction of the electron-withdrawing atoms to the acyloxy group shifts the equilibrium to the form **III**. Increasing the temperature causes further shift of this equilibrium to the right.

0022-328X/93/$6.00

$$2(EtBO)_3 + 3(RCO)_2O \xrightarrow{A} \boxed{3[Et(RCOO)B]_2O} \xleftarrow[-6EtH]{B} 6RCOOH + 3(Et_2B)_2O$$

$R = CH_3$ $R = CHCl_2, CH_2Cl, CCl_3$

(A) 100°C, 10 h; (B) heptane, reflux, 3 h.

Scheme 1.

TABLE 1. Characterization of diacyloxydiethyldiboroxanes

Compound $[Et(RCOO)B]_2O$	R	Method	Yield [a]	M.p. [b]	δ ^{11}B NMR [c] (ratio)	
1	CH_3	A	87	102–104	9.0	
2	CH_2Cl	B	83	83– 85.5	10.2	34.5 (trace)
3	$CHCl_2$	B	79	57– 60.5	11.8	34.5 (trace)
4	CCl_3	B	60	51– 54	15.2	34.5
					(15 :	1)
					17.1 [d]	34.4 [d]
					(5 :	1)

[a] Unoptimized yield (%) after crystallization; raw products were obtained quantitatively in method A and B; [b] The melting point in °C, uncorrected; [c] 96.3 MHz, in C_6D_6, at RT unless otherwise noted; [d] at 60°C.

References

1 R. Köster, *Pure Appl. Chem.*, *49* (1977) 765.

2 B. M. Mikhailov and V. A. Vaver, *Zh. Obshch. Khim.*, *31* (1961) 574 (Engl.: p. 528).

3 J. Goubeau and H. Lehmann, *Z. Anorg. Allg. Chem.*, *322* (1963) 224.

4 R. Köster, H. Bellut and W. Fenzl, *Liebigs Ann. Chem.*, (1974) 54.

5 B. M. Mikhailov and N. S. Fedotov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, (1958) 857 (Engl.: p. 832).

6 B. M. Mikhailov and T. A. Shchegoleva, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, (1958) 860 (Engl.: p. 835).

7 W. Gerrard, M. F. Lappert and R. Shafferman, *J. Chem. Soc.*, (1958) 3648.

8 R. Köster and W. Fenzl, *Inorg. Synth.*, *22* (1983) 196.

9 B. M. Mikhailov and T. A. Shchegoleva, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, (1959) 1393 (Engl.: p. 1345).

10 R. Köster and A. Sporzyński, to be published.

11 *Methoden der Organischen Chemie* (Houben-Weyl), XIII/3a, Organobor Verbindungen 1, Georg Thieme Verlag, Stuttgart, 1982, p. 828.