Tetrahedron Letters, Vol. 33, No. 20, pp. 2761-2764, 1992
Printed in Great Britain

0040-4039/92 $5.00 + .00
Pergamon Press Ltd

Simple Conversion of Anhydrides of Boronic and Borinic Acids to the Corresponding Organodihaloboranes and Diorganohaloboranes

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Key Words: organodihaloboranes; diorganohaloboranes; borinic anhydrides; boronic anhydrides; trihaloboranes

Abstract: *The reaction of the anhydrides of boronic or borinic acids with trihaloboranes in hydrocarbon solvents leads to the clean exchange of the oxygen and halide to form the organodihaloboranes and diorganohaloboranes in good to excellent yields.*

Organodihaloboranes and diorganohaloboranes are well established in their importance in organic synthesis.[1-7] A number of procedures have been reported for the preparation of organohaloboranes. The earlier methods involved the halogenation of trialkylboranes with either a halogen[8-10] or hydrogen halide.[11] Organohaloboranes have also been prepared by the reaction of a trihaloborane with an alkyne or alkene.[12] The reaction of organometallics, such as tetraalkylorganotins and trihaloboranes, has also been reported to yield the alkylhaloboranes.[13,14] The organodihalo- and diorganohaloboranes can also readily be formed by hydroboration, using the commerically available monohaloborane-dimethyl sulfides ($BH_2X{\cdot}SMe_2$) and dihaloborane-dimethyl sulfides ($BHX_2{\cdot}SMe_2$).[15-17] Alkylhaloboranes have also been formed from the redistribution of trialkylboranes with BBr_3 or BCl_3, in the presence of a catalytic amount of borane (BH_3 or $BH_3{\cdot}SMe_2$).[18-21] Borinic esters have been converted into the corresponding dialkylhaloboranes.[22] However, this reaction requires 30% excess of the trihaloborane and must be isolated by distillation to yield the pure product. An older route that has received little attention recently is the reaction of boronic and borinic acid anhydrides with trihaloboranes to yield respectively the organodihaloboranes and diorganohaloboranes.[23-25]

Recently we have reported the transmetallation of alkenyl and alkyl groups from organozirconium complexes to various haloboranes.[26-28] For these reactions, we needed a variety of pure organohaloboranes, free of residual trihaloborane or other borane products since these boron containing materials also react with the organozirconiums. This migration appears to proceed via electrophilic exchange. The presence of coordinating ligands, such as dimethyl sulfide, inhibits the transfer of the organic groups.[27] The preparation of organohaloboranes via exchange of the anhydrides of boronic and borinic acids with trihaloboranes has a number of advantages over the other methods. The reaction appears to be general, giving acceptable yields for a variety of structurally different boranes forming the chloro- and bromoorganoboranes. The corresponding anhydrides are readily formed by the dehydration of the acids. There are a variety of methods that can be used to prepare boronic and borinic acids and esters containing hydroboratable,[29,30] non-hydroboratable[31,32] and chiral groups.[33]

Burg discovered the reaction of boronic or borinic anhydrides with boron trifluoride to yield the corresponding methyldifluoro- and dimethylfluoroboranes.[34] Later, McCusker demonstrated the generality of this reaction with other trialkylboroxines to yield a variety of monoalkyldifluoroboranes in moderate yields.[35] Shortly thereafter, Lappert used this reaction to prepare phenylchloroboranes from boron trichloride and the phenyl boronic and borinic anhydrides at low temperatures.[36] This reaction was demonstrated to be useful for the synthesis of alkyldichloroboranes[37] and aryldichloroboranes.[38] The yields in this latter reaction are limited to ca. 50-60% due to the formation of a gel-like mixture of the boronic anhydride and boron oxide[37] although no by-products were observed in the product. Laurent extended this reaction for the preparation of the primary dialkylchloroboranes.[24] In a single example, Mikhailov extended this procedure for the synthesis of primary alkyldibromoboranes.[25]

Although these reactions of boronic and borinic anhydrides and trihaloboranes appeared promising as a means of synthesizing the organohaloboranes, this method was generally carried out at low temperatures (-80 °C), frequently gave low yields of product and, except for Mikhailov, used the boron trihalide gas as the reactant. In hopes of simplifying this potentially useful reaction to form organohaloboranes, we examined the reaction of a variety of structurally different anhydrides of boronic and borinic acids with the boron trihalides in hydrocarbon solvents. Solutions of boron trichloride and tribromide in hydrocarbon or methylene chloride solvents have recently become commercially available.[39] We found that dicyclohexylborinic anhydride cleanly reacted with 0.67 equivalent of BBr_3 in pentane, rapidly forming a white precipitate and cleanly yielding the dicyclohexylbromoborane, essentially quanitatively, as did the reaction with boron trichloride. The reaction of triphenylboroxine also readily reacted with both BBr_3 and BCl_3 forming the corresponding phenyldibromoborane and phenyldichloroborane respectively. A variety of alkylfluoroboranes have been prepared using boron trifluoride gas.[34,35] However, boron trifluoride, unlike the other trihaloboranes, has a very limited solubility in hydrocarbon solvents,[40] as such these reactions were not explored. Boron trifluoride etherate which is soluble in hydrocarbon solvents shows incomplete reaction with the anhydrides of boronic and borinic acids to form the alkylfluoroboranes. The extent of this reaction could not be increased with additional amounts of boron trifluoride etherate.

$$3\ R_2B{-}O{-}BR_2 + 2\ BX_3 \xrightarrow{\text{pentane}} 6\ R_2B{-}X + B_2O_3$$

$$(RBO)_3 + 2\ BX_3 \xrightarrow{\text{pentane}} 3\ RB{-}X_2 + B_2O_3$$

The reaction does not appear to be affected by the steric bulk of the alkyl groups nor does it show differences between aryl or alkyl groups. Only in the case of the very sterically hindered anhydride of diisopinocampheylborinic acid did the reaction fail to yield the anticipated product in acceptable purity and yields. The yields of the organohaloboranes and their spectral properies are summarized in Table 1.

The boron 11 NMR spectrum shows the expected organohaloborane as the major species along with minor amounts of unidentified materials as observed at *ca.* 27 ppm, < 5%. These materials are more soluble in methylene chloride and can be precipitated by the addition of pentane. The alkylhaloborane product was isolated by decanting the clear supernate from the solid material. This solid was then washed 4 × 10 mL pentane and these clear washes were added to the precipitate free alkylhaloborane solution. The volatile materials were removed under reduced pressure. Addition of 10 mL of pentane will precipitate boron containing contaminates, if any, which can be removed at this point. The haloboranes were isolated by transferring the clear supernatant solution to another flask under nitrogen and the volatiles were removed either under reduced pressure or by atmospheric pressure distillation. In general, the products were sufficiently pure at this point as shown by ^{11}B, ^{1}H and ^{13}C NMR spectroscopy and did not warrant further purification by distillation. The yields were very good, frequently greater than 80%, with a product purity greater than 98% based on NMR spectroscopy. These organohaloboranes are mositure and air-sensitive and frequently pyrophyic and must be stored under an inert atmosphere. However, the products do not show any evidence of redistribution at room temperature over a period of 12 weeks. The purity of the organohaloboranes is dependent on the purity of the boronic or borinic anhydride. This simple high yielding method can be used for the preparation of alkyldihaloboranes and dialkylhaloboranes using the corresponding boronic and borinic acid anhydrides and the readily available boron trihalides. This route appears to be general for a variety of structurally different organoboranes. We hope that increased availability of these valuable and useful organohaloboranes will further enhance their use in organic and organometallic synthesis.

Table 1. Isolated Organohaloboranes and Spectral Data.

Alkylhaloborane	%Yield	^{11}B NMR	^{1}H NMR	^{13}C NMR
t-$BuBBr_2$[†]	55	67.6	1.13 (s)	14.13
c-$C_6H_{11}BBr_2$[21,†]	65	65.5	1.92 (m, 1 H), 1.75 (m, 4 H), 1.29 (m, 6 H)	29.18, 26.76, 26.22
n-OctylBBr_2[†]	87	64.4	1.61 (m, 2 H), 1.28 (m, 12 H), 0.88 (t, 3H, J = 6.5 Hz)	37.85(b), 31.86, 31.54, 29.34, 29.18, 26.17, 22.68, 14.08
$PhBCl_2$[41]	82	54.8	8.01 (m, 2 H), 7.47 (m 1H), 7.31 (m, 2H)	136.80, 135.7 (b), 135.00, 128.05
$PhBBr_2$[41]	80	56.9	8.17 (d, J = 7.6; 7.60), 7.60 (t, J = 7.4 Hz), 7.39 (t, J = 7.6 Hz)	137.67(b), 136.54, 135.25, 128.15
Br-9-BBN[22,†]	78	82.5	1.35 (m, 2 H), 1.91 (m, 12 H)	36.22 (b), 34.12, 22.89
(*c*-$C_6H_{11})_2BCl$[42]	95	76.7	1.71 (m, 10 H), 1.43 (m, 2 H), 1.27 (m, 10 H)	36.38 (b), 27.83, 27.24, 26.71
(*c*-$C_6H_{11})_2BBr$[21,†]	89	80.7	1.72 (m, 10 H), 1.43 (m, 2 H), 1.29 (m, 10 H)	38.63 (b), 28.16, 27.03, 26.60

† Acceptable spectrum were obtained and are in agreement with expected and related products.

Acknowledgement: We thank the donors of The Petroleum Research Fund, adminstered by the American Chemical Society for support of this research.

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(Received in USA 12 December 1991; accepted 24 February 1992)