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Methyl Group Migration in the Preparation of *o*-Tolyl- and *p*-Xylyldichloroboranes

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In the preparation of *o*-tolyldichloroborane and *p*-xylyldichloroborane migration of the methyl group *ortho* to the BCl_2 group occurred. The evidence suggests that rearrangement occurs in a transition state in which the BCl_2 group is only weakly bonded to the aromatic system.

We have recently reported the preparation of some novel organoboron halides,[1] made in the course of the systematic preparation of a wide range of aryldihaloboranes.[2] In the same work some novel rearrangement reactions involving the migration of a methyl group from a position *ortho* to a dichloroboron group were discovered and are the subject of the present communication.

We have used two methods[3,4] for the preparation of *o*-tolyldichloroborane from *o*-bromotoluene, both involving the *o*-tolyl Grignard reagent. In the first route[3] the Grignard reagent is first converted into the corresponding arylmercury chloride from which the product is obtained by the action of boron trichloride. The second route[4] involves the reaction of the Grignard reagent with tri-*n*-butyl borate followed by hydrolysis, to give the *o*-tolylboronic acid. Dehydration gave *o*-tolylboronic anhydride which was heated at 150° in an atmosphere of refluxing boron trichloride.

Examination of the reaction products revealed that the first procedure gave a product which was 95% *o*-tolyldichloroborane and 5% *m*-tolyldichloroborane. The second procedure gave a product which was *ca.* 40% *o*-tolyldichloroborane and 60% *m*-tolyldichloroborane.

In the attempted preparation of *p*-xylyldichloroborane the method of Muetterties[5,6] was followed with minor modifications. In this a mixture of aluminum powder, aromatic hydrocarbon, boron trichloride, and activators of methyl iodide and iodine are heated together in an autoclave. The product was *ca.* 90% *m*-xylyldichloroborane, the other 10% being the *ortho* isomer.

It is well known that Lewis acids in the presence of hydrogen halide catalyze the isomerization of alkyl-substituted benzene derivatives. Detailed study on these systems[7-9] supports the general mechanism proposed by McCaulay and Lien[10] and it seems natural to seek a generalization of their mechanism to cover the isomerizations reported in this paper.

The important step in McCaulay and Liens' mechanism is the protonation of the aromatic hydrocarbon; it is the complex so formed which is believed to rearrange

$$\mathrm{Ar} + \mathrm{HX} \longrightarrow \mathrm{ArH^+X^-} \qquad (1)$$

It is pertinent to note that in our reactions there will be negligible quantities of hydrogen halide[6] so that equilibrium 1 is probably unimportant. This view is supported by the finding that in the attempted preparation of the *p*-xylylboron dichloride negligible rearrangement of the unreacted hydrocarbon occurs. This is important also because it helps us to select the vital rearrangement step in a heterogeneous reaction mixture of some complexity.

The following evidence may be adduced.

(1) Heating a mixture of *o*- and *m*-tolylboron dichlorides at 100° for 8 days did not change the isomer ratio, while heating the same mixture at approximately the same temperature in an atmosphere of refluxing boron trichloride for 7 hr led to a marked decrease in the percentage of *ortho* isomer (79% instead of 95%), but there was little change in the percentage of the *meta* isomer. We conclude that boron trichloride does not bring about rearrangement but it may increase the *meta*:*ortho* ratio by preferential reaction with the *ortho* isomer, particularly if the over-all yield is apparently low.

(2) A mixture of *o*- and *m*-xylyldichloroboranes showed no time dependence in its proton nmr spectra although the mixture was repeatedly heated to 100°.

(3) The possibilities of isomeric mixtures existing in the aryl halide and hydrocarbon starting materials and of rearrangement prior to reaction with boron trichloride were excluded by proton nmr studies on these materials.

The above evidence suggests that rearrangement occurs in steps involving actual reaction with boron trichloride.

(4) No mixture of isomers was obtained in the preparation of the *m*- and *p*-tolyl- and the *o*-(3,4-dimethyl)- and *m*-(3,5-dimethyl)xylyldichloroboranes, al-

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[1] C. A. Eggers and S. F. A. Kettle, *Inorg. Chem.*, **6**, 160 (1967).

[2] C. A. Eggers and S. F. A. Kettle, to be published.

[3] W. Gerrard, M. Howarth, E. F. Mooney, and D. E. Pratt, *J. Chem. Soc.*, 1582 (1963).

[4] (a) J. E. Burch, W. Gerrard, M. Howarth, and E. F. Mooney, *ibid.*, 4916 (1960); (b) P. A. McCusker and H. S. Makowski, *J. Am. Chem. Soc.*, **79**, 5185 (1957).

[5] E. L. Muetterties, *ibid.*, **81**, 2597 (1959).

[6] E. L. Muetterties, *ibid.*, **82**, 4163 (1960).

[7] M. Kilpatrick, J. A. S. Bett, and M. L. Kilpatrick, *ibid.*, **85**, 1038 (1963).

[8] R. H. Allen and L. D. Yats, *ibid.*, **81**, 5289 (1959).

[9] H. C. Brown and H. Jungk, *ibid.*, **77**, 5579 (1955).

[10] D. A. McCaulay and A. P. Lien, *ibid.*, **74**, 6246 (1952).

though the reaction conditions employed were exactly similar. This suggests that isomerization may be the result of steric crowding around vicinal ring positions, the degree of isomerization being dependent on the severity of reaction conditions.

Since the one common denominator relating all three preparations is that of a chloroboron group entering *ortho* to a methyl group, it is reasonable to suggest that the three rearrangements occur by related mechanisms. The experimental data suggest that isomerization occurs in the preparative step involving boron trichloride and that the resultant mixture of isomers is due to methyl group migration rather than variation in the position of attack by the boron halide (an alternative does not exist in the case of the *p*-xylyl compound, where rearrangement is more extensive).

It is pertinent to note that in all of the rearrangements the major (in the *o*-tolyl preparations, the only) isomerized product found is that in which the methyl group is in a position *meta* to the dichloroboron group suggesting that an electron-withdrawing (and thus a *meta*-directing) dichloroboron group once in the ring regulates the position taken up by the migrating methyl group. The 10% of *ortho* isomer found in the *p*-xylyl preparation might be explained in terms of the high lability of a methyl group in a reaction requiring comparatively violent conditions. It therefore appears that the rearrangements most probably occur in a transition state involving the aromatic system and boron halide such that the outgoing groups are partially released. So, for example, in the reaction between boron trichloride and *o*-tolylmercuric chloride one may picture this transition state as follows. The outgoing molecule $HgCl\cdots(Cl)$ temporarily blocks the 1 position, while the $BCl_2\cdots(Cl)$ unit removes electron density from both the C–Hg and C–CH_3 bonds (the BCl_2 group, which we presume to be bent and in a singlet spin state, has two formally empty orbitals, one pure p and the other a mixture of s and p). This labilization of the 2 position no longer occurs when the BCl_2 group is trapped in the 1 position. This mechanism is related to that of McCaulay and Lien[10] in that they both invoke transition states involving strongly electron-withdrawing groups acting upon a C–CH_3 bond. However, a difference arises in that our mechanism requires that the transition state complex detailed above has some finite independent existence, (*i.e.*, it may be an intermediate) since all rearrangements must occur within its lifetime. It is possible to devise reaction schemes in which this limitation does not occur, but these alternatives lack the generality of that described above.

Experimental Section

Preparation of *o*-Tolyldichloroborane. (1) **Arylmercuric Halide Route.**—To the Grignard reagent made from magnesium (10.4 g) and *o*-bromotoluene (73.0 g) in ether (200 ml) was added mercuric chloride (116.0 g), and the mixture was refluxed for 2 hr after the reaction had subsided. After hydrolysis the resultant solid was extracted with and recrystallized from chloroform. Drying *in vacuo* for 1 day yielded *o*-tolylmercuric chloride (78 g). Into 43.0 g of the latter in refluxing benzene (200 ml) boron trichloride was passed and refluxed from a condenser held at −78° for 4 hr. At the end of this time excess boron trichloride was allowed to escape. Mercuric halide was filtered from the cooled solution and the product (20 g, 50%) was obtained by distilling at *ca.* 47° (0.15 mm). A small amount of mercuric chloride also collected was completely removed by storing the product at 0° for several weeks followed by centrifuging. Comparison of both integrated nmr and infrared spectra of a prepared mixture of the *ortho* and *meta* compounds with that of a sample produced by the above reaction showed the latter to be a 19:1 mixture of *ortho* and *meta* compounds. Repeated fractionation gave a small quantity of the pure *ortho* isomer. *Anal.* Calcd for $C_7H_7BCl_2$: C, 48.6; H, 4.1. Found[11] (*ortho* isomer): C, 46.6, 46.5; H, 3.6, 4.1.

(2) **Boronic Anhydride Route.**—The Grignard reagent made from magnesium (14.2 g) and *o*-bromotoluene (100.0 g) in THF (300 ml) was brought into reaction with tri-*n*-butyl borate (160.0 ml) by simultaneous addition of the reactants to cold (−78°) stirred THF solvent (500 ml). After addition had been completed, the solution was allowed to warm to room temperature and hydrolyzed, and the solid was repeatedly extracted with hot water. The combined aqueous and THF layers were evaporated to imminent crystallization. The boronic acid (27.2 g) was dehydrated *in vacuo* to give *o*-tolylboronic anhydride (23.5 g). No reaction was apparent between the anhydride (20.0 g) and refluxing boron trichloride (25 ml) at room temperature after 3 hr and so the solid anhydride was heated gradually to 150° (3 hr) at which temperature reaction proceeded rapidly. Some carbonization occurred. Excess boron trichloride was allowed to escape and volatiles were distilled from the reaction vessel. Fractionation of the products gave a 3:2 mixture of *m*- to *o*-tolyldichloroborane (bp 84–85° (1 mm)), 11.7 g (32%), together with several fractions consisting of complex mixtures of hydrocarbons. Multiple refractionations led to the isolation of small quantities of the pure components. The composition of the reaction product was established by nmr and by measuring its dipole moment: calculated for a 3:2 mixture, 2.205 D.; found, 2.204 D. (The dipole moments of the pure components were found to be 1.995 D. for *ortho* and 2.343 D. for *meta*, all measurements being made in carbon tetrachloride solution at 25°.[12])

In both of the above preparations it was established by proton nmr that in none of the intermediates had rearrangement occurred. In the case of the boronic anhydride this was done by first reconverting it into the boronic acid.

To determine whether the isomerization of *o*- to *m*-tolyldichloroborane could occur by heat alone, a sealed nmr tube containing some of the 19:1 isomer mixture was heated at 100° and its proton nmr spectrum was run on alternate days. The experiment was discontinued after 8 days, there being no detectable difference between the original and final spectra.

The same mixture of isomers was refluxed for 7 hr at *ca.* 100° in an atmosphere of refluxing boron trichloride. At the end of this time the integrated intensity of the methyl peak associated with the *ortho* isomer accounted for only *ca.* 79% of the absorption in this spectral region. Other peaks at τ 7.24 (9%), 7.42 (5%), and 7.81 (weaker than but close to and integrated with the *meta* peak at τ 7.83 (7%)) are not found in the spectra of any tolyl- or xylylboron chloride that we have prepared and are presumably to be associated with hydrocarbon decomposition products.

Attempted Preparation of *p*-Xylylboron Dichloride.—Muetterties has described a method for the preparation of aryldichloroboranes[5,6] in which aromatic hydrocarbon, aluminum powder, and boron trichloride in the molar ratio of 4:1:2 in the presence of activators were heated in an autoclave. Using *p*-xylene as the hydrocarbon and heating at 150° for 1 hr, no hydrolyzable product was obtained. Raising the temperature effected no improvement. The variables in the preparation were

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(11) Carbon analyses in the presence of boron are usually low: A. D. Ainley and F. Challenger, *J. Chem. Soc.*, 2176 (1930).

(12) A report containing full details of these and other dipole moment measurements is in preparation.

systematically altered and it was found that a reactant weight ratio of *ca.* 2.5:1:4 heated for 2–2.5 hr at 150° maximized the yield, although this was still only moderate. So, from *p*-xylene (30.0 ml), aluminum (10.0 g), boron trichloride (40.0 g), and 0.1 g of methyl iodide and 0.1 g of iodine as activators after multiple fractionation at 0.4–0.5 mm and 65–70°, 8 g of product was obtained. The presence of a small amount of unreacted aluminum at the end of the reaction indicated the absence of appreciable concentrations of HCl during the reaction.

The nmr spectrum of the product indicated that the product was a 9:1 ratio of the *meta* (3,5-dimethyl) to *ortho* (3,4-dimethyl) isomers. It was not found possible to separate them, but the mixture analyzed correctly. *Anal.* Calcd for $C_8H_9BCl_2$: C, 51.4; H, 4.9. Found: C, 49.8; H, 4.9. Further, the dipole moment of the mixture, 2.517 and 2.519 D., the two measurements being on samples from different preparations, agrees well with that calculated, 2.506 D. (The dipole moment of the pure *o*-xylyl compound is 2.681 D. and that of the pure *meta* isomer 2.487 D., all measurements being made in carbon tetrachloride solution at 25°.[13]) Pure *ortho* and *meta* isomers were made by Muetterties' method[5,6] (xylene:boron trichloride: aluminum weight ratio of *ca.* 2:2:1, heating at 150° for 1 hr); no rearrangements occurred in these preparations.

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Chemistry of Boranes. XXXII.[1] Borane Carbonyls as Acylating Agents; Bis-Boranyl Ketones

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The reaction of 1,10-$B_{10}Cl_8(CO)_2$ with N,N-dimethylaniline has given 1,10-$B_{10}Cl_8[COC_6H_4N(CH_3)_2]_2{}^{2-}$. The reactions of various carbonyl derivatives of $B_{10}H_{10}{}^{2-}$ with $B_{10}H_{10}{}^{2-}$ and several of its derivatives have given a series of bis-boranyl ketones, exemplified by $(CH_3)_2SB_{10}H_8COB_{10}H_9{}^{3-}$. The carbonyl groups in these ketones are exceedingly basic, and the anions are customarily isolated as salts of protonated species, *e.g.*, $(CH_3)_2SB_{10}H_8COHB_{10}H_9{}^{2-}$.

A diverse chemistry has previously been reported for carbonyl derivatives of $B_{10}H_{10}{}^{2-}$ and $B_{12}H_{12}{}^{2-}$.[1–5] Carbonyls such as 1,10-$B_{10}H_8(CO)_2$, 1,10-$B_{10}Cl_8(CO)_2$, $B_{12}H_{10}(CO)_2$, and 1,6-$(CH_3)_2SB_{10}H_8CO$ have been used as intermediates to carboxyl,[2–5] isocyanate,[2–4] hydroxymethyl,[1] nitrile,[2,3] and other derivatives of the B_{10} and B_{12} cage anions. They have also been treated with organomercurials to obtain acyl derivatives.[3] Acyl derivatives had previously been obtained[5,6] by the reaction of aromatic acid halides with $B_{10}H_{10}{}^{2-}$ and had been shown[6] to have ketonic properties

$$1,10\text{-}B_{10}Cl_8(CO)_2 \xrightarrow{(C_2H_5)_2Hg} 1,10\text{-}B_{10}Cl_8(COC_2H_5)_2{}^{2-}\ {}^{3}$$

$$B_{10}H_{10}{}^{2-} + C_6H_5COCl \longrightarrow 2\text{-}B_{10}H_9COC_6H_5{}^{2-}\ {}^{6}$$

We wish to report that a third route to such organo-inorganic ketones consists of using borane carbonyls as acylating agents for active organic aromatic compounds. Furthermore, these carbonyls acylate the B_{10} cage to give a series of bis-boranyl ketones. The first type of acylation is exemplified by the reactions of 1,7-$B_{12}H_{10}(CO)_2$ and 1,10-$B_{10}Cl_8(CO)_2$ with N,N-dimethylaniline

$$1,10\text{-}B_{10}Cl_8(CO)_2 \xrightarrow{C_6H_5N(CH_3)_2} 1,10\text{-}B_{10}Cl_8[COC_6H_4N(CH_3)_2]_2{}^{2-}$$

$$1,7\text{-}B_{12}H_{10}(CO)_2 \xrightarrow{C_6H_5N(CH_3)_2} 1,7\text{-}B_{12}H_{10}[COC_6H_4N(CH_3)_2]_2{}^{2-}$$

These anions can be isolated as inner salts, *e.g.*, 1,10-$B_{10}Cl_8[COC_6H_4NH(CH_3)_2]_2$, or as normal salts. The infrared carbonyl stretching frequencies for $[(CH_3)_4N]_2$-1,10-$B_{10}Cl_8[COC_6H_4N(CH_3)_2]_2$ and Cs_2-1,7-$B_{12}H_{10}[COC_6H_4N(CH_3)_2]_2$ are at 1620 and 1600 cm^{-1}, respectively. A value of 1615 cm^{-1} was previously reported[6] for $[(CH_3)_4N]_2B_{10}Cl_9COC_6H_5$.

The reaction of 1,10-$B_{10}H_8(CO)_2$ with $(NH_4)_2B_{10}H_{10}$ proceeds smoothly in acetonitrile to give, after work-up in aqueous solution, $B_{10}H_9COB_{10}H_8COOH^{4-}$. However, the ketocarbonyl group in this inorganic ketone is extremely basic; the isolated salts of this anion are invariably protonated so that a more realistic representation of this species is $B_{10}H_9COHB_{10}H_8COOH^{3-}$

$$B_{10}H_8(CO)_2 + B_{10}H_{10}{}^{-2} \xrightarrow{-H^+} [B_{10}H_9COB_{10}H_8CO^{3-}] \xrightarrow[-H^+]{H_2O}$$

$$B_{10}H_9COB_{10}H_8COOH^{4-} \overset{H^+}{\rightleftharpoons} B_{10}H_9COHB_{10}H_8COOH^{3-}$$

Titration in water of the conjugated acid of this anion shows the presence of three strongly acidic protons, one weakly acidic, and one very weakly acidic, in agreement with this representation. Similar protonated species and their preparations include

$$B_{10}H_8(CO)_2 + B_{10}H_9S(CH_3)_2{}^{-} \longrightarrow (CH_3)_2SB_{10}H_8COHB_{10}H_8COOH^{2-}$$

$$B_{10}Cl_8(CO)_2 + B_{10}H_8[S(CH_3)_2]_2 \longrightarrow [(CH_3)_2S]_2B_{10}H_7COHB_{10}Cl_8COOH^{-}$$

$$(CH_3)_2SB_{10}H_8CO + B_{10}H_{10}{}^{2-} \longrightarrow (CH_3)_2SB_{10}H_8COHB_{10}H_9{}^{2-}$$

$$(CH_3)_3NB_{10}H_8CO + B_{10}H_{10}{}^{2-} \longrightarrow (CH_3)_3NB_{10}H_8COHB_{10}H_9{}^{2-}$$

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