Synthesis and Testing of New Non-Halogenated Flame Retardant Polymer Additives.

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Research Objective: To synthesize and test non-halogenated flame retardant polymer additives with high charring, condensed phase mechanisms of flame retardancy. These materials would be a new advanced class of flame retardants for plastics, hopefully giving superior flame resistance to existing polymer resins and materials.

Approach: A prime cause of death and injury during aircraft crashes is leakage of fuel into the fuselage, after which the fuel ignites, killing the passengers by flame or by asphyxiation from noxious fumes released. Due to the large amount of various plastic or polymeric materials found in aircraft, the need to make these materials slow burning or flame resistant in the event of an aircraft crash is therefore of great importance. One way to flame retard polymeric materials is to use high-charring compounds, or compounds which cause the polymer to char in the presence of a flame. Our approach has addressed a new class of fire-safe materials based on soluble and processable small molecule, oligomeric, and polymeric compounds that are high in carbon content and contain boron and/or phosphorus, and are free or low in halogen content. These materials, through their condensed phase cross-linking and/or charring mechanisms should give flame retardancy to polymer resins.

Accomplishment Description: A series of new alkyne-, phosphorous-, and boron-based based compounds have been developed that act as flame retardants giving V-0 results for polycarbonate (PC) in the UL-94 test without the need for brominated flame retardants. The materials discussed below showed the most effective flame retardancy when compounded into polymer resins. All of these materials synthesized had good to excellent thermal stability, with high char yields. The specific UL-94 data for each compound is shown below, with the synthetic schemes of these molecules included at the end. The materials of note which showed some flame retardancy were oligomeric carbonate **8**, phosphate **11**, and polyphosphate **15**. It was found that **8** alone showed some flame retardancy, but not as good as the bromides alone. The bromide (Br) source used for these studies was an oligomeric brominated carbonate (the starting material for **8**). This same bromide in 1 and 0.5 wt% loadings alone in PC did not give V-0 results during the UL-94 test. Oligomeric carbonate **8** and the bromide worked together to give flame retardancy to PC. With phosphate **11** and polyphosphate **15**, flame retardancy was seen. 1,4-benzenediboronic acid (**BDBA**) has shown UL-94 V-0 flame retardancy in PC with only 5 wt % loading. <u>This diboronic acid has also shown some flame retardancy in acrylonitrile-butadiene-styrene (ABS) by extending the flame burning to over 5 minutes! Large amounts of char, especially char which could not be reignited in the case of ABS, were observed when **BDBA** was used as a flame retardant.</u> The results obtained from UL-94 testing are shown below.

UL-94 Burn Results for Polycarbonate Blends With **8**, **11**, **15** and **BDBA**

Additive	1st Ignit.[a]	Drip?[b]	2nd Ignit.[a]	Drip?[b]	UL-94 Rating
5wt% **8** + 0.5wt% Br	2, 2	N, N	7, 8	N, N	V-0
10wt% **11**	7, 2	N, N	6, 5	N, Y	V-0
10wt% **15**	3, 3	N, N	3, 8	Y ,Y	V-0
5wt% **BDBA**	5, 7	N, N	9, 9	N, N	V-0

UL-94 Flame Test Results For 1,4-Benzene diboronic acid (**BDBA**)/ABS Blends

Additive	1st Ignit.[a]	Drip?[b]	2nd Ignit.[a]	Drip?[b]	UL-94 Rating
10wt% **BDBA**	335, 320	N, N	3[c], 2[c]	N, N	?
20wt% **BDBA**	289, 295	N, N	<1[c], <1[c]	N, N	?

[a]Time to self-extinguishing in seconds after 1st or 2nd 10 sec. ignition. [b]Indicates that molten plastic did (Y) or did not (N) drip onto cotton patch underneath ignited bar during UL-94 test. [c]Char glowed for the time indicated, no actual re-ignition.

Significance: Since PC is an engineering plastic heavily used in aircraft manufacture, making PC flame retardant should improve escape times for passengers in burning aircraft. Our materials, which show flame retardancy in PC, should be able to provide flame retardancy for those existing aircraft designs that utilize polycarbonate components. Flame retardancy was achieved in PC with an alkyne-containing oligomeric carbonate and a very small amount of aromatic bromide. Flame retardancy was achieved in PC with alkyne containing phosphates and diboronic acids with no additional halogen needed to achieve this result. <u>The flame retardancy observed with ABS using diboronic acids might allow the use of ABS in aircraft manufacture, thus lowering the construction costs for future aircraft</u>.

References: - Morgan, A. B.; Tour, J. M. “Aromatic Boronic Acids. Non-halogenated Condensed-phase Flame Retardants for Acrylonitrile-Butadiene-Styrene and Polycarbonate” Submitted for publication in *Chemistry of Materials*.

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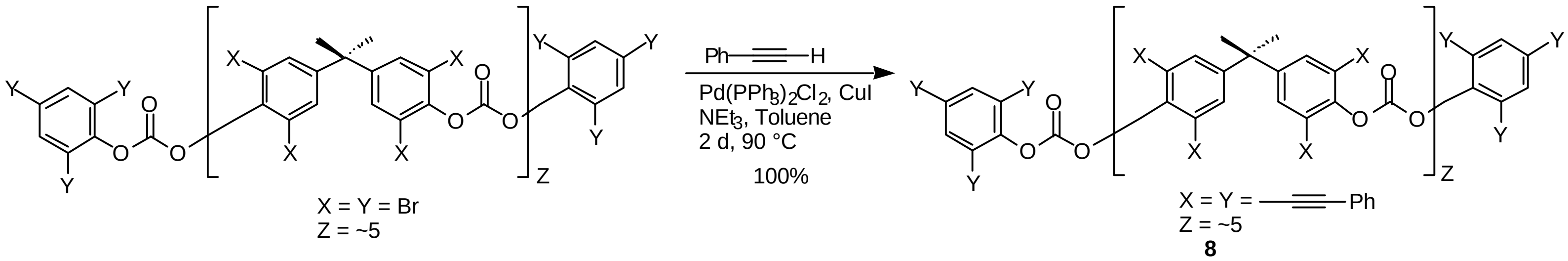
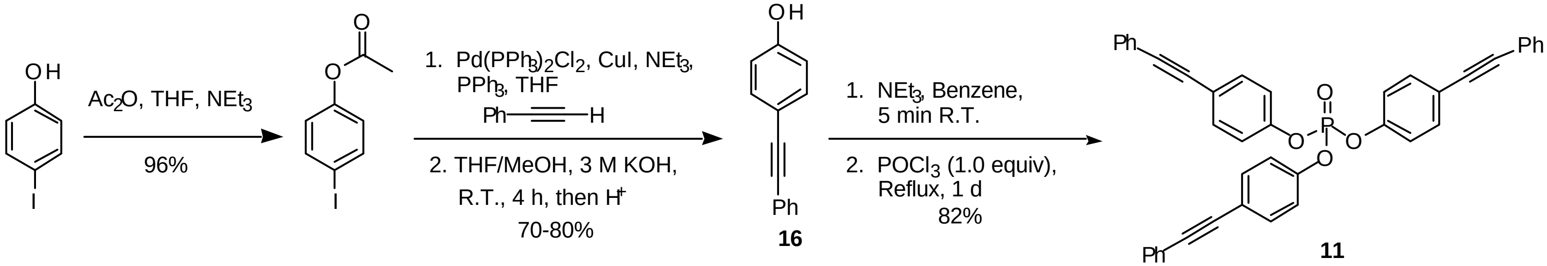
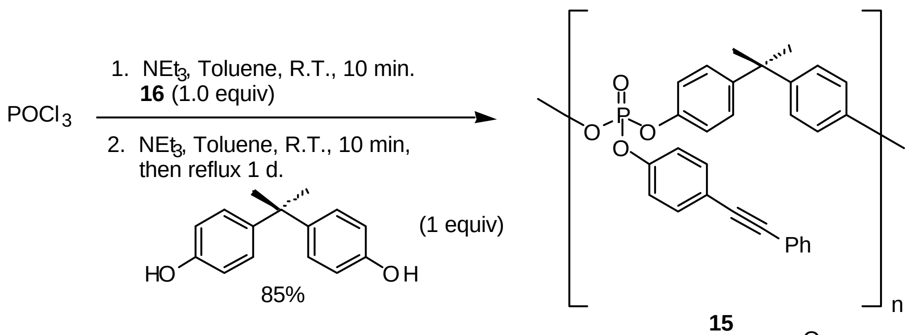
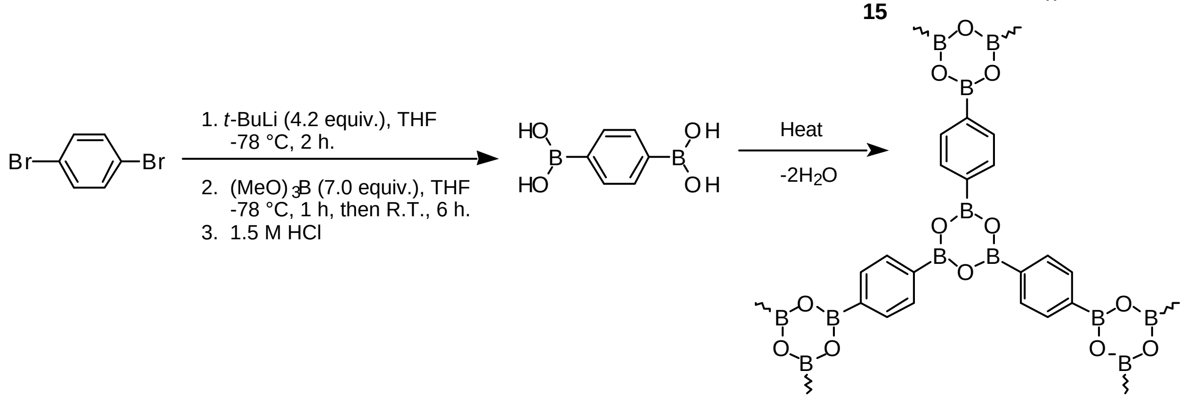
- Morgan, A. B.; Tour, J. M. “Potential Flame Retardant Polymer Additives: Synthesis of Enediynes & Polyphenylenes.” *Society of Plastics Engineers, Inc.: Technical Papers* **1996**, *42*, 3018.


Ph—≡—H
Pd(PPh3)2Cl2, CuI
NEt3, Toluene
2 d, 90 °C
100%
X = Y = Br
Z = ~5
X = Y = —≡—Ph
Z = ~5
8


Ac2O, THF, NEt3
96%
1. Pd(PPh3)2Cl2, CuI, NEt3, PPh3, THF
Ph—≡—H
2. THF/MeOH, 3 M KOH, R.T., 4 h, then H+
70-80%
16
1. NEt3, Benzene, 5 min R.T.
2. POCl3 (1.0 equiv), Reflux, 1 d
82%
11


POCl3
1. NEt3, Toluene, R.T., 10 min.
16 (1.0 equiv)
2. NEt3, Toluene, R.T., 10 min, then reflux 1 d.
(1 equiv)
85%
15


1. t-BuLi (4.2 equiv.), THF
-78 °C, 2 h.
2. (MeO)3B (7.0 equiv.), THF
-78 °C, 1 h, then R.T., 6 h.
3. 1.5 M HCl
Heat
-2H2O