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Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
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To cite this Article Sket, Boris and Zupan, Marko(1983) 'Polymer-Supported Boron Trifluoride', Journal of Macromolecular Science, Part A, 19: 5, 643 — 652
To link to this Article: DOI: 10.1080/00222338308069445
URL: http://dx.doi.org/10.1080/00222338308069445

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J. MACROMOL. SCI.–CHEM., A19(5), pp. 643-652 (1983)

Polymer-Supported Boron Trifluoride

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ABSTRACT

Polystyrene, cross-linked with 7.8% of divinylbenzene, formed a stable complex in chloroform with boron trifluoride containing 0.11% of boron, while cross-linked polystyrene-4-vinylpyridine resins containing 2-2.5% of pyridine rings formed a stable complex with boron trifluoride, containing 1.04% of boron. Both complexes catalyze conversions of aromatic aldehydes, ketones, and acids with alcohols into corresponding acetals, cyclic ketals, and esters; diphenylmethanol converts into ether. The structure of the alcohol plays an important role, with conversions decreasing in the order 1-butanol, 2-butanol, tert-butanol. Both complexes are very stable and in most cases more reactive than the cross-linked polystyrene-$AlCl_3$ complex.

Aluminum chloride and boron trifluoride are well-known catalysts which have proved to be of great use in organic chemistry. Neckers and co-workers [1] have demonstrated that cross-linked polystyrene forms stable complex with $AlCl_3$, which is less sensitive to moisture and is stable more than 1 year. On the other hand, boron trifluoride is a very toxic reagent and must be handled with care. Boron

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0022-233X/83/1905-0643$3.50/0

trifluoride forms stable complex with diethylether and the resulting solution is much easier to handle than BF_3 alone, but changes of chemical reactivity were also observed.

In our continuing interest in the preparation of halosubstituted organic molecules [2], we found it relevant to prepare boron trifluoride complexes with polymer resins and to study their reactivity.

Saturation of chloroform, containing polystyrene, cross-linked by 1.8% of divinylbenzene, with boron trifluoride at 0°C showed no changes in the polymer resins. Further, we have investigated the possible influence of the degree of cross-linking on BF_3-polystyrene complex formation. We prepared a series of polystyrenes, with 4.2, 6.6, 7.8, 8.8, and 13.4% cross-linking, and found that the 7.8% cross-linked resin is the only one leading to the formation of a complex, and it contained 0.11% of boron. The IR spectra of polystyrene and the polystyrene-BF_3 complex are presented in Fig. 1. We have also found that the amount of BF_3 on the polymer backbone increases by a factor of 10 when 2% of the benzene rings in the polystyrene resins are replaced by pyridine. The IR spectrum of the BF_3 complex with cross-linked (1.8%) copolymer of polystyrene-4-vinylpyridine, containing 2-2.5% of pyridine rings, is presented in Fig. 1.

The chemical reactivity of the boron trifluoride complex with polystyrene (2A) and polystyrene-4-vinylpyridine (2B) was studied in the reactions of aromatic aldehydes with alcohols in benzene as solvent. The substrates for the reaction were chosen in such a manner as to enable comparison of the reactivity with those catalyzed by the $AlCl_3$ complex (2C) [3]. Reactions of benzaldehyde (1, X = H, Scheme 1) with 1-butanol (3A) in the presence of 2A, 2B, 2C, polystyrene (2D), and without the catalyst are summarized in Table 1. The results demonstrate that BF_3 complexes are more reactive than the polystyrene-$AlCl_3$ complex [3]. We have further investigated the effect of the substituent bonded to the aromatic ring on acetal formation, and found that electron-withdrawing groups enhance the reactivity while electron-donating groups retard the reaction. The greater reactivity of BF_3 complexes compared to the polystyrene-$AlCl_3$ complex was again confirmed in almost all cases. The structure of the alcohol has a significant role on acetal formation: conversions of starting aldehyde (1, X = p-NO_2) are very high with 1-butanol (3A), diminishes in the case of 2-butanol (3B), while the reaction fails in the case of tert-butanol (3C). The conversions of aldehyde to acetal were in some cases also enhanced by the presence of polystyrene, as is evident from Table 1.

Complexes 2A and 2B have also been found to activate the formation of cyclic ketals (Scheme 2). The effect of ring size of the cycloalkanone (5) and the structure of the diol (6) on conversion to ketal is presented in Scheme 2. The BF_3 complex with polystyrene-4-vinylpyridine (2B) is slightly more reactive than the complex with polystyrene (2A).

The BF_3 complex with polystyrene-4-vinylpyridine (2B) is also active in the transformation of progesterone (8, Scheme 3) into cyclic ketals [5] (9 and 10), formed in the ratio 4:1.

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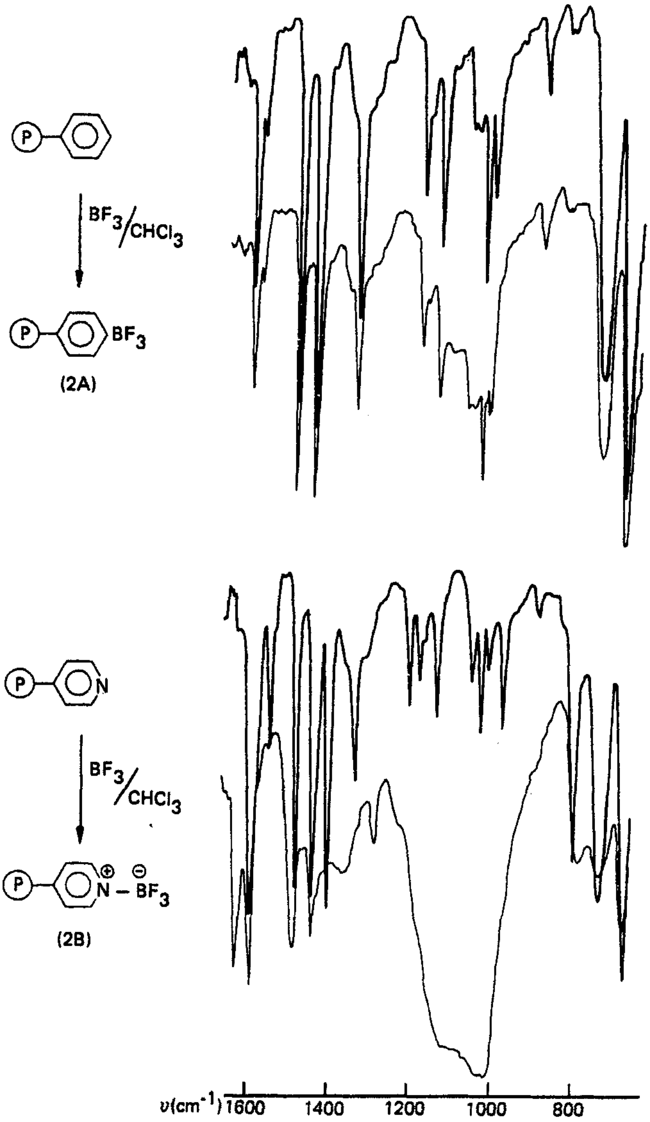
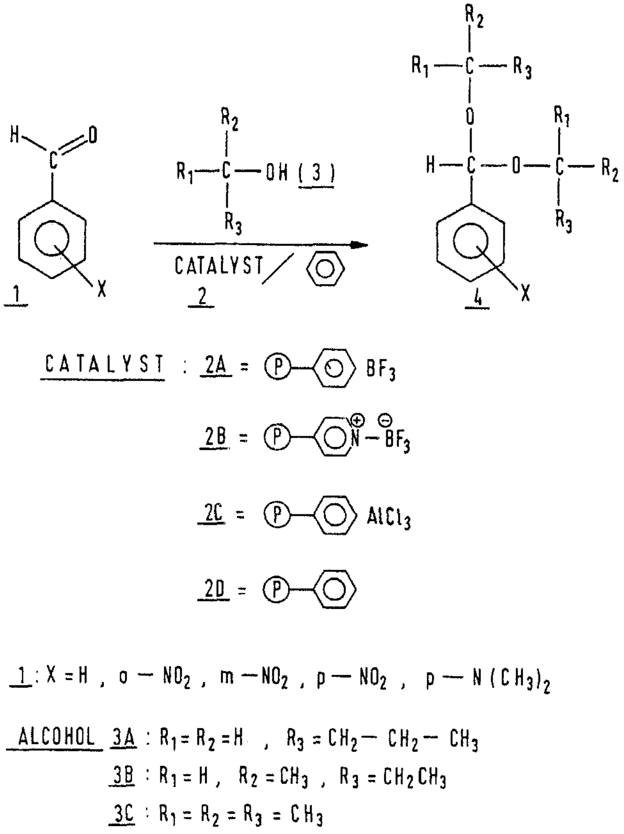


FIGURE 1.



SCHEME 1.

Diphenylmethanol (11, Scheme 3) is quantitatively converted to ether (12) in benzene solution in the presence of the BF_3 complex with polystyrene-4-vinylpyridine (2B).

Finally, we have studied polymer-supported catalyst activity for the transformation of acids (13, Scheme 4) into esters (14). Results presented in Scheme 4 are consistent with those already found, i.e., the greater reactivity of the BF_3 complexes (2A, 2B) compared to the $AlCl_3$ complex (2C) is again confirmed [4].

After all the reactions are carried out in the presence of BF_3 complexes (2A and 2B), catalysts need only be washed with chloroform and can be reused. The loss of activity is, in the case of 2A, 10-15%, and in the case of 2B, 10%. The BF_3 complex with polystyrene-4-vinylpyridine (2B) can be used at least five times, while both

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TABLE 1. Effects of Variables on Acetal Formation

Aldehyde	Alcohol	Catalyst	Time (min)	Conversion (%)[a]
1, X = H	3A	2A	30	64
		2A	120	69
		2A	300	72
		2B	120	70
		2C	150	21[b]
		2D	120	16
		-	120	6
	3B	2A	120	-
		2B	120	-
		2C	5.520	-[b]
1, X = o-NO$_2$	3A	2A	30	89
		2A	120	95
		2B	120	96
		2C	1080	62[b]
1, X = m-NO$_2$	3A	2A	30	43
		2A	120	89
		2B	120	90
1, X = p-NO$_2$	3A	2A	30	94
		2A	120	95
		2B	120	97
		2C	1440	48[b]
		2D	120	20
		-	120	-
	3B	2A	120	25
		2B	120	27
		2D	120	-
	3C	2A	120	-
		2B	120	-
1, X = p-N(CH$_3$)$_2$	3A	2A	300	-
		2B	300	-

[a] All reactions under reflux in benzene; determined by ^{1}H-NMR.
[b] Ref. 3, yield determined by VPC.

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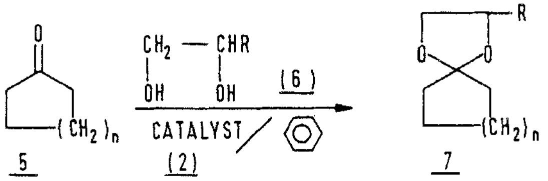
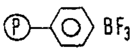


$\underline{5A}$: n = 1
$\underline{5B}$: n = 2
$\underline{5C}$: n = 3

$\underline{6A}$: R = H
$\underline{6B}$: R = CH_3

CATALYST	R	n	% CONVERSION [a)]
 2A	H	1	61
		2	94
		3	50
	CH_3	1	98
		2	96
		3	65
 2B	H	1	63
		2	95
		3	53
	CH_3	1	98
		2	97
		3	67

a) ALL REACTIONS UNDER REFLUX FOR 120 min IN BENZENE ; DETERMINED BY ^1H NMR

SCHEME 2.

catalysts can be regenerated after loss of activity. Polymer resins are first stirred in sodium hydroxide solution for 2 h at 40°C, then washed with water and a series of solvents, dried, and finally transformed into the BF_3 complex. Catalysts 2A and 2B are not sensitive to moisture and can be stored in polyethylene bottles for at least 2 years. All the reactions with Catalysts 2A and 2B can be carried out in a glass vessel.

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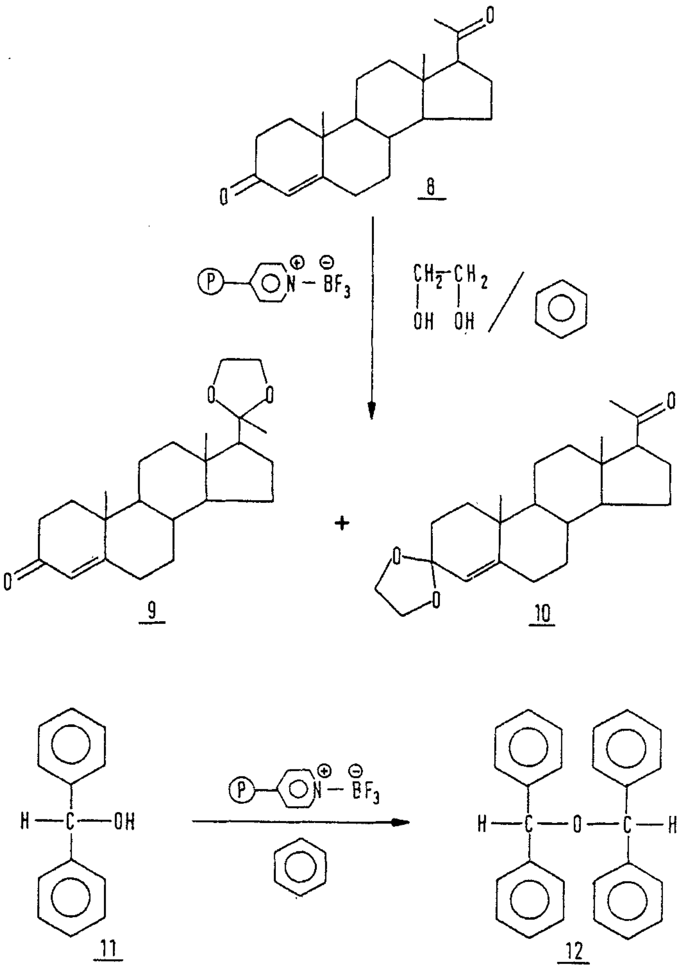

SCHEME 3.

EXPERIMENTAL

Preparation of Boron Trifluoride Complex with Cross-Linked Polystyrene (2A)

20 g of cross-linked polystyrene (7.8% of divinylbenzene) was suspended in 200 mL of chloroform, left to swell for 3 h at room temperature, and boron trifluoride was introduced with stirring at 0°C

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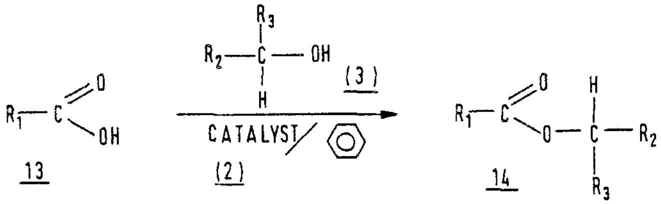
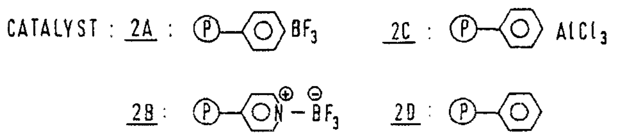


13A : $R_1 = CH_3$ 3A : $R_2 = H$, $R_3 = CH_2-CH_2-CH_3$

13B : $R_2 = CH_2CH_3$ 3B : $R_2 = CH_3$, $R_3 = CH_2-CH_3$



ALCOHOL	ACID	CATALYST	CONVERSION (%) [a)]
3A	13A	2A	66
		2B	68
		2D	—
		—	—
	13B	2A	100
		2B	100
		2C	70[(b)]
		2D	12
		—	7
3B	13B	2A	—
		2B	—
		2C	36[(b)]
		2D	—

a) ALL REACTIONS UNDER REFLUX FOR 120 min IN BENZENE; DETERMINED BY ^1H NMR

b) REF. 4, YIELD DETERMINED BY VPC

SCHEME 4.

until saturation was reached. After 20 min, boron trifluoride was again introduced and the reaction mixture was stirred for another 20 minutes at 0°C. The polymer was filtered off, washed with chloroform, dried for 24 h at room temperature, and 22.2 g of boron trifluoride complex (2A) was isolated. For the following reactions the catalyst was used without further drying. Three hours of drying of 1 g of 2A at 100°C gave 0.92 g of polymer, containing 0.11% of boron.

Preparation of Boron Trifluoride Complex with Cross-Linked Polystyrene-4-vinylpyridine (2B)

20 g of cross-linked polystyrene-4-vinylpyridine (containing 2-2.5% of pyridine rings) was suspended in 200 mL of chloroform, left to swell for 3 h at room temperature, and boron trifluoride was then introduced with stirring at 0°C until saturation was reached. After 20 min boron trifluoride was again introduced and the reaction mixture was stirred for another 30 min at 0°C. The polymer was filtered off, washed with chloroform, dried for 24 h at room temperature, and 23.4 g of BF_3 complex (2B) was isolated. For the following reactions the catalyst was used without further drying. Three hours of drying of 1 g of 2B at 100°C gave 0.89 g of polymer, containing 1.04% of boron.

GENERAL PROCEDURE

Formation of Acetals (4)

10 mmol of aldehyde (1) and 50 mmol of alcohol (3) were dissolved in 10 mL of benzene and 0.5 g of catalyst (2A, 2B, or 2D) was added. The reaction mixture was heated under reflux for various times (noted in the table), polymer beads were filtered off, the solvent was evaporated in vacuo, and the residue was poured into 20 mL of water. Acetal (4) and unreacted aldehyde (1) were extracted with chloroform, the chloroform layer dried over Na_2SO_4, filtered off, the solvent evaporated in vacuo, and the reaction mixture analyzed by ^{1}H-NMR spectroscopy. Results are presented in Table 1. Pure products were isolated by VPC or TLC and characterized on the basis of spectroscopic data: ^{1}H-NMR, IR, and mass data were compared with those in the literature.

Formation of Ketals (7)

10 mmol of ketone (5) and 10 mmol of diol (6) were dissolved in 10 mL of benzene and 0.5 g of Catalyst 2A or 2B was added. The reaction mixture was heated under reflux for 120 min, polymer beads were filtered off, the solvent evaporated in vacuo, and the residue was analyzed by ^{1}H-NMR spectroscopy. The conversions of ketones are listed in Scheme 2. Pure products were isolated by preparative VPC and characterized on the basis of spectroscopic data: ^{1}H-NMR, IR, and mass spectra were compared with those in the literature.

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Formation of Esters (14)

10 mmol of acid (13) and 20 mmol of alcohol (3) were dissolved in 10 mL of benzene and 0.5 g of Catalyst 2A, 2B, or 2D was added. The reaction mixture was heated under reflux for 120 min, polymer beads were filtered off, and the residue was analyzed by ^{1}H-NMR. The conversions of acids are listed in Scheme 4. Pure products were isolated by preparative VPC and characterized on the basis of spectroscopic data: ^{1}H-NMR, IR, and mass spectra were compared with those in the literature.

Formation of Ether (12)

10 mmol of diphenylmethanol (11) was dissolved in 10 mL of benzene and 0.5 g of Catalyst 2A, 2B, and 2D was added. The reaction mixture was heated under reflux for 2 h, polymer beads were filtered off, the solvent was evaporated in vacuo, and the residue was analyzed by ^{1}H-NMR. Alcohol was quantitatively transformed into ether, while no conversion was observed when polystyrene (2D) was used. The structure of the product was characterized on the basis of spectroscopic data: ^{1}H-NMR, IR, and mass data were compared with those in the literature.

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Accepted by editor July 1, 1982
Received for publication July 12, 1982

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