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Application of poly(vinylphenyltrimethylammonium tribromide) resin as an efficient polymeric brominating agent in the α -bromination and α -bromoacetalization of acetophenones

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ABSTRACT

The applications of a new supported tribromide reagent based on poly(vinylbenzyltrimethylammonium hydroxide) resin (Amberlite 717) were reported. This supported tribromide resin was used directly in α -bromination and α -bromoacetalization of acetophenones without any other catalyst under mild conditions. The effects of solvents and the amount of the supported tribromide resin on the reactions were investigated. Under the optimal conditions, most of α -bromo and α -bromoacetal of acetophenones were selectively obtained in excellent yields.

GRAPHICAL ABSTRACT



R: H, *p*-Br, *p*-Cl, *m*-Br, *o*-Cl, *p*-NO₂, *m*-NO₂, biphenyl, 4'-Br-biphenyl, *p*-Me, *p*-MeO. cyclohexanone, 3-pentanone

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KEYWORDS

α-Bromination; α-bromoacetalization; tribromide resin; polymeric brominating agent

Introduction

Development of a safe, simple, and efficient synthetic method for the widely used key organic intermediates from commercially available reagents is one of the major challenges in organic synthesis. α -Bromo and α -bromoacetal of acetophenones are significant synthons used for the synthesis of a variety of biologically active heterocyclic compounds, especially triazole fungicides,^[1] α , β -unsaturated ketones,^[2] and enol ether.^{[2}c[]] A number of various bromination protocols of carbonyl compounds have been developed, including the use of molecular bromine or its complexes in the presence of protic or Lewis acid.^[3] Alternative brominating agents, such as copper(II) bromide,^[4] *N*-bromo reagents,^[5] dioxane-dibromide,^[6] and organic ammonium tribromides

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(OATB),^[7] have been increasingly used for α -bromination of carbonyl compounds resulting in easier handling and increased selectivity of the reaction. Organic ammonium tribromides are preferable owing to hazards associated with bromine and the other advantages are involving their solid form, high stability, maintenance of desired stoichiometry and mild reaction condition. Hitherto, several organic ammonium tribromides have been reported, such as tetramethylammonium tribromide,^[8] tetrabutylammonium tribromide,^[9] pyridinium tribromide,^[10] phenyltrimethylammonium tribromide.^[11] However, recovery and recycling of expensive quaternary ammonium salts are also poor during the post-processing, and in some cases, a substantial quaternary ammonium salts get extracted along with the organic products.

Anion exchange resin is a kind of insoluble polymer, and the utilization of it as supports in the organic synthesis has acquired a wide interest in recent years,^[12] because of the ease of work-up and product purification, and minimized environmental damages.^[13] Amberlite 717 (CAS: 9002-24-8, poly(vinylbenzyltrimethylammonium hydroxide)^[14] is one of the strongly basic anion exchange resins, which has been extensively used as a disinfectant for industrial and domestic water^[15] and is much cheaper than quaternary ammonium salts. For example, the price of Amberlite 717 was about ten times lower than that of benzyltrimethylammonium bromide and seven times lower than tetramethylammonium bromide in 2019, according to the product catalog of Aladdin.

Herein, to overcome the problem of high cost, recovery, and recycling of organic ammonium bromides reagents, we wish to report the applications of Poly(vinylbenzyltrimethylammonium tribromide) (PVBMATB) resin from Amberlite 717, as a novel polymeric brominating agent in the α -bromination and one-pot α -bromoacetalization of acetophenones.

Results and discussion

Organic ammonium tribromides represent an important class of bromination reagents, which are more stable than the liquid bromine because of their crystalline nature, and hence their storage, transport, and use are easy. However, production of these reagents utilizing volatile organic molecular bromine and ammonium bromide is unsafe for human health and the environment. There are a few interesting reagents like NH₄Br-LDH-WO₄^{2-,[16]} HBr-H₂O₂,^[17] NaBr-NaIO₄,^[18] KBr-selectfluoro,^[19] KBr-oxone,^[20] and NaBr-NaBrO₃,^[21] which have been developed to afford bromohydrins and their derivatives.

Amberlite 717 (Poly(vinylbenzyltrimethylammonium hydroxide) is a common strongly basic anion exchange resin, which was brought directly from Aladdin. It was changed to bromide form through exchange reaction with an aqueous solution of HBr (3 equiv.). And then, poly(vinylphenyltrimethylammonium bromide) resin was treated with 1/3 equiv. of KBrO₃, and the color of resin converted from golden to red. After filtration, poly(vinylbenzyltrimethylammonium tribromide) resin (PVBMATB) was obtained with almost 100% yield (Scheme 1 and Figure 1). The capacity of the PVBMATB resin was determined isometrically to be 2.5 mmol/g of resin. Interestingly the resin could be stored for 1 year in a glass dryer without any loss of its activity.

In the preliminary experiments, our initial objective was to identify an appropriate solvent for regioselective α -monobromination of acetophenone with PVBMATB resin.



Scheme 1. Preparation of poly(vinylbenzyltrimethylammonium tribromide) resin(PVBMATB resin).



Figure 1. Amberlite 717 resin(poly(vinylbenzyltrimethylammonium hydroxide) supported tribromide.

Table 1. Effect of solvents on the α -bromination of **1a** with PVBMATB resin^a.

Entry	Solvent	Selectivity(2a/3a/4a/1a) ^b
1	THF	22/0/0.2/78
2	CH_2CI_2	51/0/16/33
3	CH₃CN	30/0/35/35
4	CH₃OH	63/13/4/20
5	C ₂ H ₅ OH	46/11/12/42
6	(CH ₃) ₂ CHOH	52/0/15/39
7	Ethylene glycol	40/24/2/34

 a The reaction was performed with 2.5 mmol of acetophenone (1a), 1.0 g of PVBMATB resin, 5 mL of solvent at 30 $^\circ$ C for 6 h.

^bThe ratio of 2a/3a/4a/1a was determined by GC.

Entry	$V_{\rm Methanol}/V_{\rm water}(\rm mL)$	Selectivity(2a/3a/4a/1a) ^b
1	3/2	42/0/8/50
2	4/1	57/0/14/30
3	4.4/0.6	82/0/6/12
4	4.5/0.5	92/0/8/0
5	4.7/0.3	76/0/6/18
6	4.9/0.1	65/0/7/28

Table 2. Effect of water on the α -bromination of 1a with PVBMATB resin^a.

^aThe reaction was performed with 2.5 mmol of acetophenone (1a), 1.0 g of PVBMATB resin, 5 mL of the mixture of methanol and water at 65 $^{\circ}$ C for 1 h.

^bThe ratio of **2a/3a/4a/1a** was determined by GC.

For this purpose, acetophenone **1a** was chosen as the test substrate for the reaction with 1 g of PVBMATB resin in various solvents and the results are summarized in Table 1. When tetrahydrofuran (THF), CH_2Cl_2 , or CH_3CN was used as a solvent, the reaction completed within 6 h to give low reaction activity of α -monobromination. In the above study, the best results were observed in methanol. For example, using methanol as a solvent, the selectivity of **2a** could reach 63/4 (entry 4, Table 1). However, 13% of α -bromoacetal of acetophenone were observed. When ethylene glycol was used, 24% of α -bromoacetal of acetophenone(2-bromomethyl)-2-phenyl-1,3-dioxolane, **3a**) were observed (entry 5, Table 1).

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Entry	m _{PVBMATB} resin (g)	Selectivity(2a/4a/1a) ^b
1	0.8	74/2/24
2	0.9	87/11/2
3	1.0	92/8/0
4	1.1	84/12/0
5	1.2	80/14/0

Table 3. Effect of PVBMATB resin on the α -bromination of acetophenone **1a**^a.

^aThe reaction was performed with 2.5 mmol of acetophenone (1a), 5 mL of the mixture of methanol and water at 65 $^\circ$ C for 1 h.

^bThe ratio of 2a/4a/1a was determined by GC.

Table 4. Effect of PVBMATB resin on the α -bromoacetalization of **1a** in ethylene glycol^a.

Entry	m _{PVBMATB} _{resin} (g)	Yield of 3a
1	0.8	59
2	0.9	65
3	1.0	74
4	1.1	97
5	1.2	83

^aThe reaction was performed with 2.5 mmol of acetophenone (1a), 5 mL of ethylene glycol at room temperature for 24 h.

Secondly, it was essential to reduce the α -bromoacetalization and improve the α -bromination reactivity of acetophenone. When a little water was added to the reaction system, the product of α -bromoacetalization of acetophenone determined by GC disappeared (Table 2). So, the amount of water was further investigated. we found that a mixture of 0.5 mL of water and 4.5 mL of methanol was the best solvent for the maximum selectivity of the desired product **2a** (92:8) at 65 °C for 1 h (entry 4, Table 2).

The effect of PVBMATB resin (g) on the α -bromination of acetophenone (1a, 2.5 mmol) was also investigated (Table 3). When 0.8 g of PVBMATB resin was added to the reaction mixture and the ratio of the α -monobromination product was only 74% (entry 1, Table 3). Increased the amount of PVBMATB resin to 1.0 g, the ratio could increase to 92% (entry 3, Table 3). When a larger amount PVBMATB resin was added, the α,α -dibromination product increased rapidly. The optimal α -bromination condition for yield generation requires 2.5 mmol of 1a, 1g of PVBMATB resin, 4.5 mL of methanol, and 0.5 mL of water at 65 °C for 1 h.

When the reaction was performed in the presence of ethylene glycol, PVBMATB resin could transform from acetophenone to the corresponding α -bromoacetal derivatives without any other catalyst. The effects of amount of PVTATB (g) to acetophenone (1a, 2.5 mmol) on the rate of reaction were investigated, and the results were summarized in Table 4. The optimum amount (g) of PVBMATB resin to acetophenone (mmol) was found to be 1.1:2.5.

To investigate the scope of these protocols, the optimized conditions of α -bromination and α -bromoacetalization were then applied to the synthesis of a variety of substituted acetophenones. The results are listed in Table 5. When 1b and 1c with a halogen atom on the para-position of benzene ring, were selected, the yields of 2b and 2c were 96 and 95%, respectively (entries 2 and 3, Table 5), and 3b and 3c were 91 and 96%, respectively. When 2-chloroacetophenone (1d) was used as the tested substrate, the yields of α -bromination and α -bromoacetalization were only 60 and 85% (entries 4, Table 5), which could be attributed

	R 1 1 PVBMATB resin methanol or ethylene glycol		Br 4 Minor
Entry	Substrate	Product 2, Yield(%)	Product 3, Yield(%)
1		Br 2a, 91	Br 3a, 97
2	Br 1b	Br Br 2b, 96	Br Br 3b, 91
3		cr 2c, 95	ci Br 3c, 96
4	C 1d	CI 2d, 60	G 3d, 85
5	O ₂ N 1e	O ₂ N Br 2e, 77	0 ₂ N Br 3 e , 96 ^c
6		^O ₂ N, Br 2 f , 89	0 ₂ N, Br 3f , 93 ^c
7		2g, 97	3g , 96°
8	Br 1h	Br 2h, 96	Br 3h, 95°
9	li	Br 2i, 91	3i, 88
10	H ₃ CO lj	H ₃ CO Br 2 j , 93	Meo Br Br 3j, 97
11		$\mathbf{\mathbf{k}}_{N} \mathbf{\mathbf{k}}_{\mathbf{k}} \mathbf{\mathbf{k}} \mathbf{\mathbf{k}}_{\mathbf{k}} \mathbf{\mathbf{k}}_{\mathbf{k}} \mathbf{\mathbf{k}} \mathbf$	_e
12		^o Br 21, 53	oBr 31,92
13	1m	Br 2m , 87	осо Вг 3m , 90

Table 5. $\alpha\text{-Bromination}$ and $\alpha\text{-bromoacetalization}$ of 1 with PVBMATB resin^{a,b} .

^d^d² equiv. of PVBMATB resin was added.

 $^{^{}a}\alpha$ -Bromination was performed with 2.5 mmol of 1, 1.0 g of PVBMATB resin, 5 mL of the mixture of methanol and water at 65 °C for 1 h; α -bromoacetalization was performed in 5 mL of ethylene glycol at room temperature for 24 h. ^bIsolated yield.

^eThe product was too complex for further separation.

to the steric effect of ortho-chlorine atom. When 2e and 2f was prepared from 1e and 1f with a strong electron-withdrawing group (-NO₂) on the benzene ring, the yields were only 77 and 89%; however, the reactivity of α -bromoacetalization (1e and 1f) was very low, it may be the result of the low solubility of 1e and 1f in ethylene glycol at room temperature. So, when the reaction temperature was increased to $45 \,^{\circ}$ C, **3e** and **3f** could be obtained with excellent yields (96 and 93%) (entry 5 and 6, Table 5); the same process was also used to prepare 3g and 3h, the yields of α -bromoacetalization were 96, and 95%, respectively (entries 7, and 8, Table 5), respectively. When 1i, with an electron-donating group (-CH₃) on the benzene ring, was tested, both α -bromination and α -bromoacetalization were also good, with the yields of 2i and 3i reaching 91 and 88%, respectively (entries 9, Table 5). In the case of substrates with a strong electron donation group $(-OCH_3)$, such as 1j, the product of α -bromination (2j) could reach 93%, however, the main product of α -bromoacetalization was 2bromomethyl-2-(3-bromo-4-methoxyphenyl)-1,3-dioxolane (3j), and the yield was 97% when 2 equiv. of PVBMATB resin was added (entry 10, Table 5). In our new chemical processes, α -bromination and α -bromoacetalization of acetophenones with electron-withdrawing or electron-donating groups on the para-position of benzene ring were preformed in excellent yields. When 2-acetylpyridine (1k) was tested, α -bromination products of 2k could be obtained with a 96% yield, and the α -bromoacetalization was too complex to further separation (Entry 11, Table 5). Cyclohexanone (11) and 3-pentanone (1m) were also selected as test substrates, 2l, 2m, 3l, and 3m could be obtained with 53, 87, 92 and 90% yields, respectively (entry 12, and 13, Table 5).

Finally, in all of these applications workup of the reaction was easy. When the reaction was completed, the color of the resin turned from red to golden, and the resin of poly (vinyl-phenyltrimethylammonium bromide) could be recycled from the reaction mixture via simple filtration. The recovered resin could be converted into their tribromide form in very high yield as stated in the experimental part. It was also observed that the recycled resin, after recycling at least 3 times, could be used without any loss in the efficiency.

In summary, we developed a simple and green method to prepare poly(vinylbenzyltrimethylammonium tribromide) resin from Amberlite 717 with the aqueous solution of HBr and KBrO₃, and demonstrated that the resin is a useful novel polymeric brominating reagent in the α -bromination and bromoacetalization of acetophenones without any other catalyst. In the proposed system, the *in situ* generation of HBr from the reaction of PVBMATB resin and acetophenones catalyzed the α -bromination and caused further acetalization of the reaction. The advantages of PVBMATB resin are: low price of raw materials, stability, high efficiency, simple filterability and reusability, and the reaction processes have confirmed its high application value.

Experimental section

Representative procedure for preparation of poly(vinylbenzyltrimethylammonium tribromide) resin

Amberlite 717 (10 g, 50 wt%) was washed three times with 30 mL of deionized water. The resin was added to an aqueous solution of HBr (65 mL, 10%) for 5 h, and then an aqueous solution of KBrO₃ (1.5 g, 9 mmol) was added to the mixture over a period of 30 min. The reaction took place immediately and the solution became yellow with a

concurrent golden resin of poly(vinylbenzyltrimethylammonium bromide) supported tribromide. The red resin with tribromide (PVBMATB resin) was filtered, washed 3 times with water and dried in a glass dryer at room temperature. The isolated yield of PVBMATB resin was almost 100%. The recycling procedure of the recovered resin was the same as the preparation of PVBMATB resin.

Representative procedure for preparation of α -bromoacetophenone

A mixture of 2.5 mmol of **1a**, 4.5 mL methanol, and 0.5 mL of water was stirred for 5 min, and then 1 g of PVBMATB resin was added, and the mixture was stirred 1 h at 65 °C. Afterward, the resin of poly(vinylbenzyltrimethylammonium bromide) was recycled through filtration and washed with ether. The combined organic layer was washed twice by water (20 mL), and dried over anhydrous Na₂SO₄. After filtration, the solvent was removed under reduced pressure, and the residual was treated with silica gel column chromatography (Petroleum ether/AcOEt = 20/1, ν/ν) to generate the product. **2-bromo-1-phenyl ethanone** (**2a**):^[22] Yield 91%, white solid; m.p.: 48–50 °C (lit: 48–49 °C); ¹H NMR (500 MHz, CDCl₃) δ 4.44 (s, 2H, CH₂Br), 7.60–7.62 (m, 2H, ArH), 7.68–7.70 (m, 1H, ArH), 8.00–8.03 (m, 2 H, ArH). IR (KBr, cm⁻¹): 3055, 3002, 2953, 1694, 1598, 1449, 1390, 1283, 1198, 1092, 993, 746, 687, 624.

Representative procedure for preparation of α -bromoacetal of acetophenone

A mixture of 2.5 mmol of **1a**, and 5 mL ethylene glycol was stirred for 5 min, and then 1.1 g of PVBMATB resin was added, and the mixture was stirred 24 h at room temperature or 45 °C. Afterward, the resin of poly(vinylbenzyltrimethylammonium bromide) was recycled through filtration and washed with ether. The combined organic layer was washed twice by water (20 mL), and dried over anhydrous Na₂SO₄. After filtration, the solvent was removed under reduced pressure, and the residual was treated with alumina chromatography (Petroleum ether/AcOEt = 20/1, ν/ν) to generate the product. **2-bromomethyl-2-phenyl-1,3-dioxolane** (**3a**):^[23] Yield 97%, white solid, m.p.: 56–58 °C, ¹H NMR (500 MHz, CDCl₃) δ 3.66 (s, 2H), 3.88–3.91 (m, 2H), 4.17–4.20 (m, 2H), 7.32–7.38 (m, 3H), 7.52 (d, 2H, J=7.5 Hz); IR (KBr, cm⁻¹): 3011, 2885, 1627, 1485, 1470, 1447, 1220, 1169, 1039, 1029, 997.

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