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Convenient synthesis of triarylmethanes and 9,10-diarylanthracenes by alkylation of arenes with aromatic aldehydes using acetyl bromide and $ZnBr_2/SiO_2$

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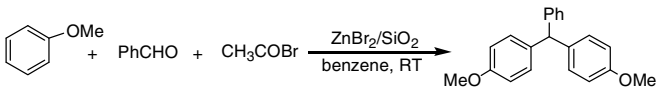
Abstract

Reaction of electron-rich arenes with acetyl bromide and aldehydes in the presence of silica gel-supported zinc bromide was carried out in benzene to give selectively the corresponding triarylmethanes or 9,10-diarylanthracenes in high yields depending upon the ratio of an arene and an aldehyde. The mild conditions employed are especially noteworthy.

Keywords: Triarylmethane; Anthracene; Aldehyde; Silica gel-supported zinc chloride

The acid-catalyzed Friedel–Crafts alkylation of arenes with aromatic aldehydes has been known since 1886.[1] The reaction using Lewis acid such as $AlCl_3$ had not received much attention until recently because of the formation of many products such as triarylmethanes, triarylmethanol, diarylmethane, and anthracene derivatives.[2] However, the analogous reaction of aldehydes has been investigated extensively. Lewis acid-catalyzed reductive Friedel–Crafts reaction of arenes with aromatic aldehydes afforded exclusively the corresponding diarylmethanes. For instance, diarylmethanes formed selectively in the reaction using $CaCl_2$,[3] $Sc(OTf)_3$/1,3-propanediol,[4] and $InCl_3$/chloromethylsilane.[5] Recently, it has been reported that the alkylation of arenes with aldehydes using catalytic $AuCl_3$/3AgOTf [6] or [Ir(COD)Cl_2/$SnCl_4$[7] gives triarylmethanes selectively. $LnCl_3$ (Ln = Pr, Dy, Er, Sm. Yb) and $Yb(OTf)_3$-catalyzed alkylation of PhR (R = H, Me) with AcCl–PhCHO also affords the corresponding triarylmethane.[8] We found that silica gel-supported zinc bromide ($ZnBr_2/SiO_2$) catalyzed alkylation of electron-rich arenes with acetyl bromide–aromatic aldehydes gave the corresponding triarylmethanes in high yields under mild conditions. Triarylmethanes have attracted the attention of chemists because of the interesting properties associated with their derivatives.[9] Although a number of methods are available for the synthesis of triarylmethanes, most of them are multistep process and/or require hash reaction conditions.[10] We wish to report herein a convenient and practical method for the preparation of triarylmethanes and 9,10-diarylanthracenes by the reaction of electron-rich arenes with AcBr and aromatic aldehydes in the presence of $ZnBr_2/SiO_2$. The reaction of anisole with benzaldehyde was carried out in the presence of $ZnBr_2/SiO_2$ at room temperature, but no products were obtained and anisole was recovered. In contrast, the reaction with AcBr and benzaldehyde in the presence of $ZnBr_2/SiO_2$ under similar conditions afforded 4,4′-dimethoxytriphenylmethane **1** in high yield.



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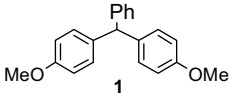
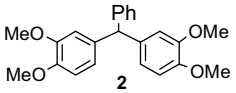
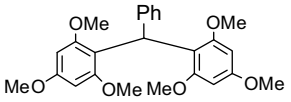
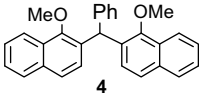
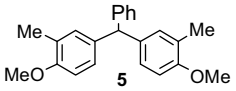
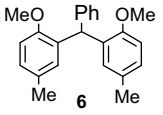
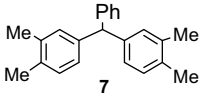
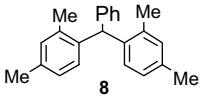
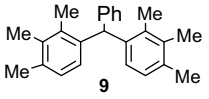
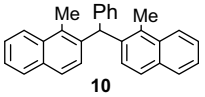
Thus, to a mixture of anisole (4 equiv), benzaldehyde (1 equiv), and $ZnBr_2/SiO_2$[11] in benzene was added dropwise, with stirring, a solution of acetyl bromide in benzene. After the addition, the slurry was stirred for 1 h at room temperature, and **1** was obtained in 84% yield. Acetylanisole which is formed from Friedel–Crafts acylation of anisole with acetyl bromide was not detected. Toluene can also be used as a solvent, whereas in polar solvent such as THF and dioxane the yield is very low. We next explored the bisarylation of benzaldehyde with various arenes for the synthesis of triarylmethanes.[12] The results are shown in Table 1.

Electron-rich arenes such as anisole, 1,2-dimethoxybenzene (veratrole), 1,3,5-trimethoxybenzene, 2- and 4-methoxytoluene, and 1-methoxynaphthalene gave the corresponding triarylmethane in high yields (entries 1–6).

Table 1
Reaction of various arenes with AcBr and benzaldehyde (PhCHO) leading to triarylmethanes[a]

Entry	Arene	Temp (°C)/time (h)	Product	Yield[b] (%)
1	Anisole	rt/1	 **1**	84
2	1,2-$(MeO)_2$-Benzene	rt/1	 **2**	94
3	1,3,5-$(MeO)_3$-Benzene	rt/0.25	 **3**	71
4	1-(MeO)-Naphthalene	rt/1	 **4**	88
5	2-(MeO)-Toluene	rt/1	 **5**	94
6	4-(MeO)-Toluene	rt/1	 **6**	90
7	1,2-Me_2-Benzene	50/3	 **7**	73
8	1,3-Me_2-Benzene	50/3	 **8**	72
9	1,2,3-Me_3-Benzene	50/3	 **9**	78
10	1-Me-Naphthalene	50/3	 **10**	97

[a] Reaction conditions: arene (8 mmol), benzaldehyde (2 mmol), acetyl bromide (4 mmol), $ZnBr_2/SiO_2$ (0.67 g, 0.8 mmol of $ZnBr_2$ on SiO_2), benzene (15 ml).
[b] Isolated yield.