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BF_3-H_2O Catalyzed Hydroxyalkylation of Aromatics with Aromatic Aldehydes and Dicarboxaldehydes: Efficient Synthesis of Triarylmethanes, Diarylmethylbenzaldehydes, and Anthracene Derivatives

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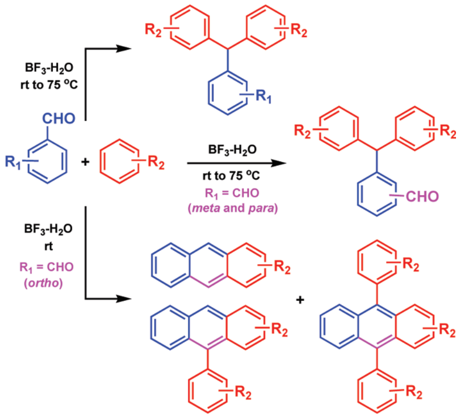

BF_3-monohydrate is found to be an efficient and strong acid catalyst as well as an effective protosolvating medium suitable for the hydroxyalkylation of arenes with aromatic aldehydes. This reaction has been extended to aromatic dialdehydes, such as terephthalic dicarboxaldehyde and isoterephthalic dicarboxaldehyde, for the efficient synthesis of diarylmethylbenzaldehydes, which are useful synthons for various organic transformations. Further, successful one step convergent synthesis of various synthetically useful anthracene derivatives from phthalaldehyde was also achieved. BF_3-H_2O is less expensive and acts as an efficient substitute for nonoxidizing strong protic acids/superacids.

Introduction

Boron trifluoride[1,2] is a well-known gaseous Lewis acid (mp −127 °C and bp −100 °C/35 mmHg). BF_3 alone or in complex form with other n-donor molecules, such as diethyl ether, dimethyl sulfide, acetic anhydride, and so on, can generate good Lewis acidic systems, and several reactions have been studied.[2] Because boron in BF_3 is highly oxophilic, complexation with protic oxygenated compounds such as alcohols can give rise to strong Brønsted acid systems.[3] Unlike other boron halides, hydrolysis of BF_3 is very slow. Meerwein in 1933 found that water can form stable complexes with BF_3 and the systems can act as Brønsted acids.[4]

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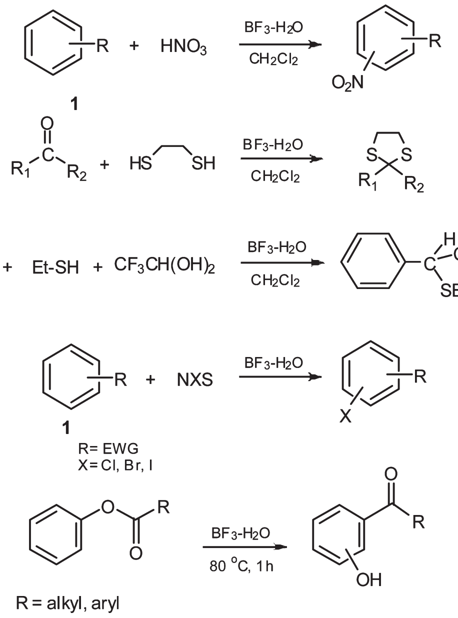
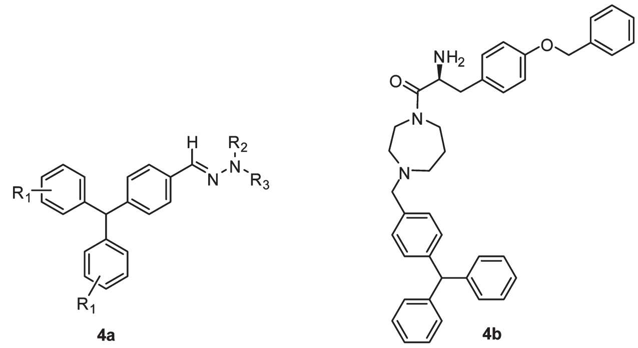
Two types of water complexes are known with BF_3: the monohydrate (BF_3-H_2O) and the dihydrate (BF_3-2H_2O) complexes. The dihydrate complex is very stable, less fuming than the monohydrate and its acidity is close to that of 100% nitric acid. On the other hand, BF_3-H_2O 1:1 complex is a strong acidic system with the acidity close to that of 100% sulfuric acid ($H_o \sim 12$).[5] These complexes can be prepared by passing BF_3 slowly into adequate amount of water with proper cooling. BF_3 monohydrate complex (colorless fuming liquid, density of 1.8 g/mL, and mp 6.2 °C) is less expensive than trifluoromethanesulfonic acid and nonoxidizing in nature like trifluoromethanesulfonic acid. These properties permit many acid-induced synthetic transformations, which were previously carried out using expensive superacids. Over the years, we found that it can act as an excellent acid system for a wide range of reactions, such as preparation of alkyl nitrates and sulfides from carbonyl compounds, thioacetalization of ketones, nitration of aromatics using potassium nitrate, halogenations of deactivated aromatics using *N*-halosuccinimides, the Fries rearrangement, and so on (Scheme 1), under mild reaction conditions.[6]

SCHEME 1. BF_3-H_2O as an Acid Catalyst in Various Organic Reactions



Since 1886, acid-catalyzed condensation reaction of aromatic aldehydes with aromatics, also known as hydroxyalkylation, has been studied extensively.[7,8] In most of the cases, this reaction required expensive superacids,[9] such as trifluoromethanesulfonic acid, Magic acid, and so on. During our ongoing efforts to introduce acid systems to replace expensive acids, we decided to study the condensation reaction of aromatic aldehydes (**2** and **3**) with various arenes using BF_3-H_2O as the catalyst. We extended this methodology to three isomeric dicarboxaldehydes-terephthalic dicarboxaldehyde (benzene-1,4-dicarboxaldehyde **3a**), isoterephthalic dicarboxaldehyde (benzene-1,3-dicarboxaldehyde **3b**), and phthalic dicarboxaldehyde (benzene-1,2-dicarboxaldehyde **3c**) under similar conditions. Reactions of **3a** and **3b** with arenes gave the corresponding diarylmethylbenzaldehydes in high yields. However, the products from phthalaldehyde (benzene-1,2-dicarboxaldehyde **3c**) are identified as anthracene derivatives. Many of these compounds are new, and the reaction of only electron-rich aromatics with dialdehydes under Lewis acid conditions have been known.[10] Diarylmethylbenzaldehyde derivatives could be useful synthons for many biologically and chemically important compounds. For example, the hydrazone derivatives (e.g., compound **4a**) of the diarylmethylbenzaldehydes are widely used as charge-transporting material for electrographic photoreceptors showing improved charge transport, increase in sensitivity, better residual potential characteristics, and better durability.[11] Compound **4b** is known to be the agonists of melanocortin receptors and shows high biological activities for the treatment, control, or prevention of diseases and disorders responsive to the activation of the melanocortin receptors[12] (Scheme 2).

SCHEME 2. Synthetic Applications of Diarylmethyl Benzaldehyde Derivatives



Charge-transporting material for electrographic photoreceptor

Agonists of melanocortin receptors

Anthracene and its derivatives are important chemical compounds, which possess diverse chemical and physical properties. They are used to make major components of electroluminescent devices and photothermographic

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(12) Poindexter, G. S.; Luo, G.; Chen, L. U.S. Pat. 232807, **2003**.

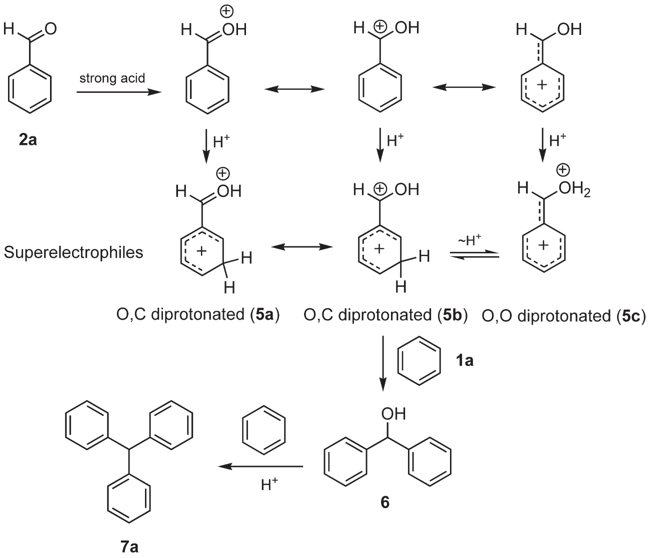
materials,[13] combination marker for liquids,[14] liquid crystals,[15] organic thin film transistors,[16] and several other commercially important substances.

Herein, we report the results of our study on the condensation reaction of aromatic aldehydes and dialdehydes with aromatics under superelectrophilic activation using BF_3-H_2O as the catalyst as well as the reaction medium.

Results and Discussion

Condensation of Aromatic Aldehydes with Aromatics. It has been shown that acid-catalyzed condensation reaction of aromatic aldehydes with aromatics initially produces diarylmethanols, which undergo further reaction with another molecule of the arene to provide the corresponding triarylmethane derivatives. The acidity dependence of this reaction has been studied and reported earlier.[9] In the presence of very strong Lewis acids such as $AlCl_3$, benzene and benzaldehyde give a mixture of products.[17] The effect of basicity of carbonyl compounds on this reaction has also been studied by Hatzsch,[18] using 100% H_2SO_4. However, this reaction does not occur to any significant degree with 100% H_2SO_4 at room temperature. This relates to the fact that formation of a highly electron-deficient species under strong protosolvolytic conditions is required as a driving force for this reaction. Carboxonium ions were first studied by Meerwein.[19] Studies on stability and reactivity of carbocations have shown the effect of neighboring group participation and its consequences on attenuating the electrophilicity of the carbocations.[20] In acid medium, if protonation occurs on the oxygen atom, the resulting cation is stabilized both by the oxygen and the neighboring phenyl group, thus making it a relatively weak electrophile. To decrease this neighboring group participation effect and increase the electrophilicity of the carbonyl carbon, further protonation of the system is required. According to Olah's definition of superelectrophiles, under superacidic conditions, further protonation or protosolvation of the protonated aldehydes is possible,[21] which leads to very reactive intermediates (superelectrophiles). This superelectrophilic or multi-ionic intermediate can undergo successive condensation reactions with weaker nucleophiles like aromatics (Scheme 3).[21b−f] Ohwada and Shudo have demonstrated the mechanistic aspects of triflic acid-catalyzed reactions of cinnamaldehyde and nitroolefins with benzene, in which many multiply charged cationic species (dicationic and tricationic) were involved.[22] Later, Olah and co-workers have carried out computational studies (ab initio calculations) on similar systems to find out the possible formation of dicationic intermediates and their properties in superacids. Their studies indicated that the most preferred dicationic intermediate is the *O*,*C*-(aromatic) dication (**5a**,**b**) and not the *O*,*O*-diprotonated system (**5c**).[7a,b] However, recent studies on zeolite-catalyzed hydroxyalkylation by Sommer et al. suggested that the intermediacy of monocationic species is also important in these reactions.[7e]

SCHEME 3. Mechanism for the Superacid-Catalyzed Condensation Reaction of Benzaldehyde with Benzene



During our previous studies using BF_3-H_2O, we found that BF_3-H_2O can act both as a strong acid catalyst and an efficient protic solvent/protosolvating medium.[6e−g] It offers optimum acidity for the halogenation of many deactivated aromatics, which are not feasible under normal acidic conditions. Intrigued by these results, we have conducted the reactions of different aldehydes with various aromatics using BF_3-H_2O under varying reaction conditions (Scheme 4). As expected, BF_3-H_2O acts as a strong acid catalyst as well as a good reaction medium for effective protosolvation of protonated aldehydes. Depending on the nature of aldehydes and the aromatics, the reaction occurs smoothly at room temperature and above, giving the triarylmethane products in good to excellent yields in most cases. It is important to note that these reactions are relatively clean making work up and purifications rather easy. Results are summarized in Tables 1 and 2. However, during the reaction of electron rich aldehydes with aromatics, we observed transformylation reaction followed by arylation. This type of phenomenon has already been reported in the literature.[23] Thus, when

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benzene was reacted with *p*-tolualdehyde, mostly triphenylmethane was formed; *p*-anisaldehyde gave a mixture of triphenylmethane and phenol; 2-naphthaldehyde gave naphthalene, 2-naphthol, and triphenylmethane.

SCHEME 4. Reaction of Aromatic Aldehydes with Aromatics under BF_3-H_2O Catalyzed Conditions

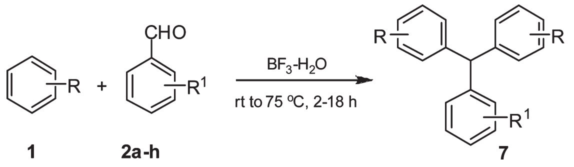
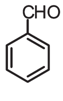
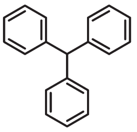
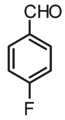
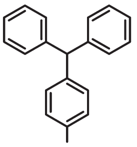
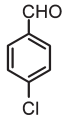
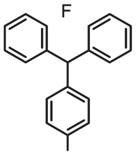
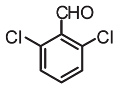
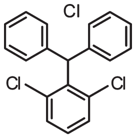
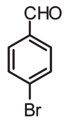
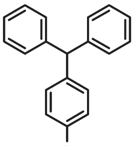
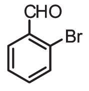
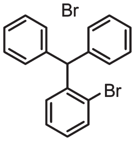
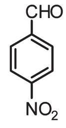
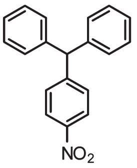
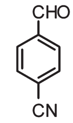
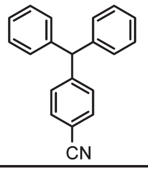


TABLE 1. Reaction of Aldehydes with Benzene under Superelectrophilic Activation

Entry	Aldehydes (**2a-h**)	Temp (°C)	Time (h)	Products (**7a-h**)	Yield (%)
a		75	2		94
b		75	2		85
c		75	2		87
d		75	2		87
e		75	2		95
f		75	2		91
g		50	2		98
h		rt	3		88

To explore the efficacy of BF_3-H_2O catalyzed hydroxyalkylation reaction, we have studied the reactions of different aromatics with benzaldehyde initially. We found that electron rich aromatics smoothly react with benzaldehyde compared to the electron deficient aromatics. Reactions of benzaldehyde **2a** with aromatics carrying electron withdrawing groups, such as halobenzenes, were sluggish. However, when benzaldehyde was replaced by an electron deficient aldehyde, such as nitrobenzaldehyde **2g**, the reaction with halobenzenes became faster and went to completion (Table 2, entries 5, 6, and 7). This clearly shows how the substrates and reaction profile can be tuned in favor of product formation at a faster rate. In the case of substituted aromatics, *para,para*-derivatives were found to be the major component in the product mixture. Highly deactivated aromatics such as nitrobenzene and dihalobenzenes do not react even with activated aldehydes under similar reaction conditions.

Even though the product is a mixture of various isomers (*para,para*-isomer as the major), chemical yields were found to be high. The condensation of aldehydes with aromatics can be carried out using BF_3-monohydrate in a dual role, as a suitable protic solvent and as an efficient catalyst, under moderate reaction conditions. Reaction works well with varieties of aldehydes and arenes. As mentioned earlier, reactions of aldehydes with electron rich aromatics are more facile compared to electron poor systems. Reactions are often very simple, clean and do not require further purification in most cases. Because the reaction worked well with aromatic monoaldehydes, studies were extended to three isomeric aromatic dialdehydes.

Condensation of Terephthalic Dicarboxaldehyde (3a) with Aromatics. Because the reaction of dicarboxaldehydes with arenes has not been explored to any significant degree, we decided to carry out a detailed study on the reactions of aromatic dicarboxaldehydes with arenes. Only a few refs[10,24] are available regarding the reaction of aromatic dicarboxaldehydes with aromatics. As early as 1886, Oppenheimer[20] mentioned that 100% H_2SO_4 can catalyze the reaction of benzene and terephthalic dicarboxaldehyde to give rise to the corresponding diarylmethyl benzaldehyde **8**. Interestingly, only one of the two aldehyde functional groups reacts under the reaction conditions. However, a detailed description of the reaction conditions was not available. When we performed the reaction using terephthalic dicarboxaldehyde and different aromatics with BF_3-H_2O as catalyst, we obtained the corresponding 4-diarylmethyl benzaldehyde derivatives (**8**) in high yields and purity (Scheme 5, Table 3). Further hydroxyalkylation using the second aldehyde functional group to obtain the tetraaryl derivative was not observed in these cases. Even after the products, diarylmethylbenzaldehyde derivatives (**8**), were separated and treated with aromatics in excess BF_3-H_2O, no products due to second hydroxyalkylation step could be detected. Presence of two arene moieties in the neighborhood could reduce the electrophilicity of the protonated carbonyl center to such an extent that further attack by a weak nucleophile (arene in this case) would not occur. Also, the effect of protosolvation occurring in the ring bearing the carbonyl function could be reduced significantly, which in turn would reduce the electrophilicity of the protonated carbonyl functional group restricting further attack by weak nucleophiles.

Electron-rich aromatics undergo reactions under ambient conditions (Table 3, entries 2, 3, 4, and 8), whereas electron poor aromatics need higher temperature for the completion of

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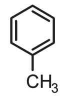
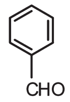
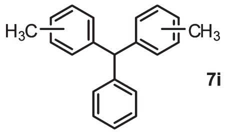
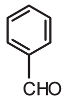
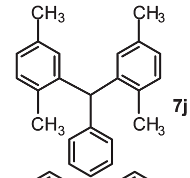
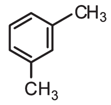
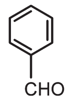
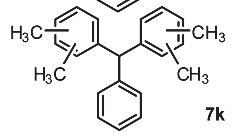
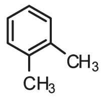
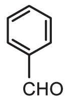
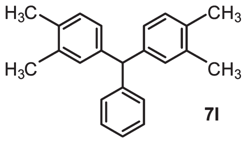
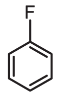
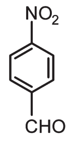
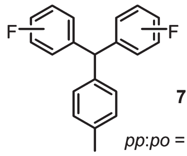
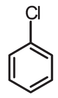
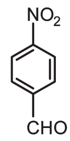
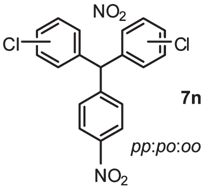
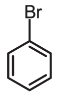
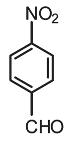
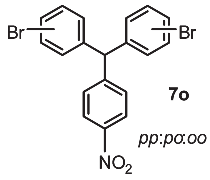
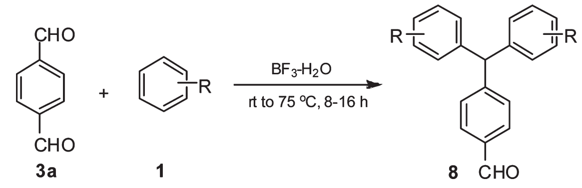
TABLE 2. Reaction of Aromatic Aldehydes with Different Aromatics under BF_3-H_2O Catalyzed Conditions

Entry	Arenes	Aldehydes	Temp. (°C)	Time (h)	Products	Yield (%)
1	 **1b**	 **2a**	50	16	 **7i** *pp*:*po*:*oo* = 78:21:1	82
2	 **1c**	 **2a**	50	16	 **7j**	87
3	 **1d**	 **2a**	50	16	 **7k** mixture of possible isomers	86
4	 **1e**	 **2a**	50	16	 **7l** 4,4:4,3:3,3 = 62:25:13	88
5	 **1f**	 **2g**	75	10	 **7m** *pp*:*po* = 90:10	95
6	 **1g**	 **2g**	85	18	 **7n** *pp*:*po*:*oo* = 77:22:1	75
7	 **1h**	 **2g**	85	18	 **7o** *pp*:*po*:*oo* = 71:21:8	73

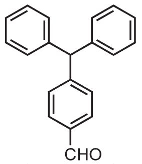
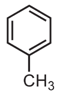
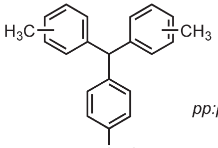
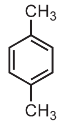
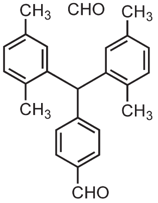
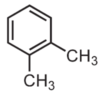
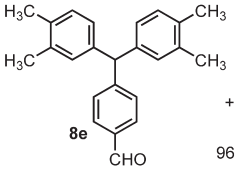
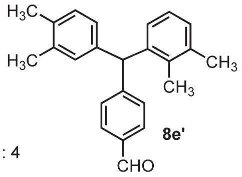
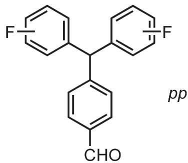
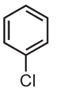
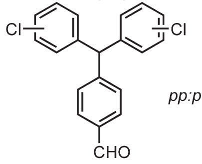
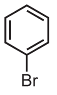
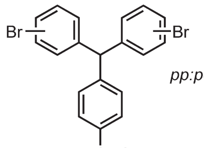
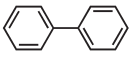
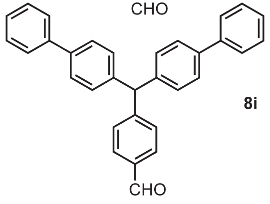
SCHEME 5. Reaction of Terephthalic Dicarboxaldehyde with Aromatics under BF_3-H_2O Catalyzed Conditions



the reaction (Table 3, entries 1, 5, 6, and 7). However, electron deficient aromatics such as dihalobenzenes and nitrobenzene do not react under the reaction conditions. In the case of substituted aromatics, *para*,*para*-derivatives were obtained as the major product, along with small amounts of other possible isomers. When the reaction was monitored carefully using GCMS at various time intervals, the progress of the reaction was found to be sequential. It was found that the initial attack of the arene to the dialdehyde was very fast, but further attack by a second molecule of arene leading to the final product was much slower. However, the reactions are very clean, giving the products in good to excellent yields in most cases.

Condensation of Isoterephthalic Dicarboxaldehyde (3b) with Aromatics. Similar to terephthalic dicarboxaldehyde (**3a**), isoterephthalic dicarboxaldehyde (**3b**) also gave the corresponding 3-diarylmethylbenzaldehyde derivatives (**9**) when treated with aromatics in BF_3-H_2O (Scheme 6). The reaction with electron-rich aromatics can be performed under ambient temperature, whereas aromatics with an electron withdrawing group require higher temperatures. However,

TABLE 3. Reaction of Terephthalic Dicarboxaldehyde (3a) with Aromatics

Entry	Arenes	Temp (°C)	Products	Yields (%)
1*	 **1a**	75	 **8a**	90
2	 **1b**	rt	 **8b** *pp:po* = 88:12	86
3	 **1c**	rt	 **8c**	75
4	 **1e**	rt	 **8e** +  **8e'** 96 : 4	85
5	 **1f**	75	 **8f** *pp:po* = 88:12	90
6	 **1g**	75	 **8g** *pp:po* = 78:22	80
7	 **1h**	75	 **8h** *pp:po* = 79:21	75
8	 **1i**	rt	 **8i**	65

*Reaction time for **1a** is 8 h, and for all other substrates, 16 h.

similar to the case of terephthalic dicarboxaldehyde, nitro and dihalogenated aromatics do not undergo the condensation reaction with isoterephthalic dicarboxaldehyde. With unsymmetrical systems mostly *para,para* derivatives were obtained with small amounts of other possible isomers. The results are shown in Table 4. The mechanism must be similar to that involved in terepthalic dicarboxaldehyde reaction.

Condensation of Phthalic Dicarboxaldehyde (3c) with Aromatics. Reaction of phthalic dicarboxaldehyde (**3c**) with

SCHEME 6. Reaction of Isoterepthalic Dicarboxaldehyde (3b) with Aromatics under BF_3-H_2O Catalyzed Conditions

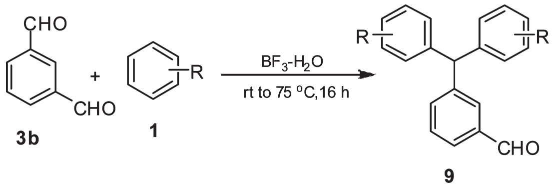
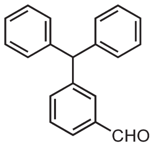
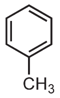
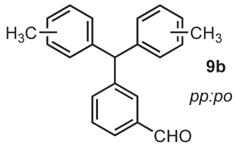
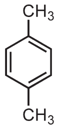
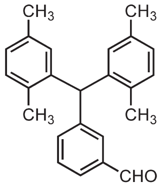
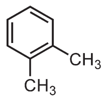
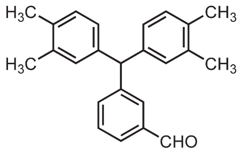
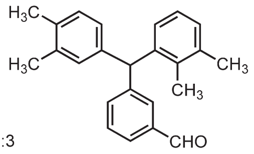
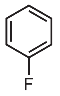
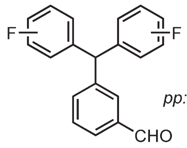
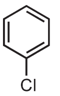
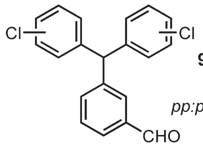
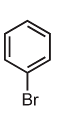
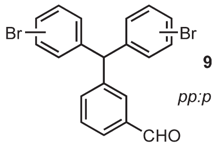
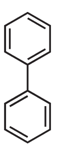
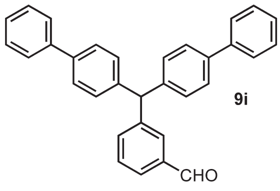


TABLE 4. Reaction of Isoterephthalic Dicarboxaldehyde (3b) with Aromatics under BF_3-H_2O Catalyzed Conditions

Entry	Arenes	Temp (°C)	Products	Yields (%)
1	 **1a**	75	 **9a**	89
2	 **1b**	rt	 **9b** *pp*:*po* = 83:17	81
3	 **1c**	rt	 **9c**	86
4	 **1e**	rt	 +  **9e** 97:3 **9e'**	82
5	 **1f**	75	 **9f** *pp*:*po* = 87:13	88
6	 **1g**	75	 **9g** *pp*:*po* = 82:18	78
7	 **1h**	75	 **9h** *pp*:*po* = 78:22	68
8	 **1i**	rt	 **9i**	60

aromatics interestingly gave anthracene derivatives as major products. Direct synthesis of anthracene derivatives is rare. Most of the methods available to synthesize anthracene derivatives are associated with mainly Suzuki coupling[25] or functional transformation of the anthracene moiety. Hence, this methodology could be useful for the synthesis of anthracene derivatives[26] **12**−**14** directly from the aromatics and phthalic dicarboxaldehyde (**3c**). We attempted the condensation with a variety of aromatics and found that the reaction works well only with electron-rich systems. With electron-deficient systems the reactions were very sluggish. The results are shown in Scheme 7. In most cases, we obtained the 9-arylanthracenes **13** as the major product. However, with

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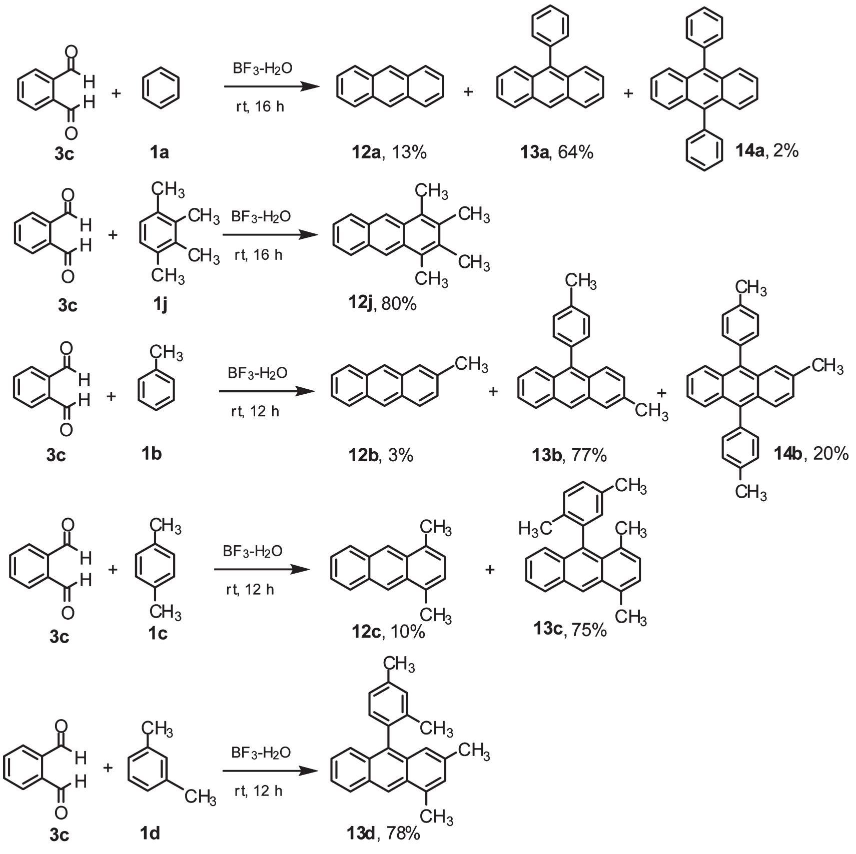
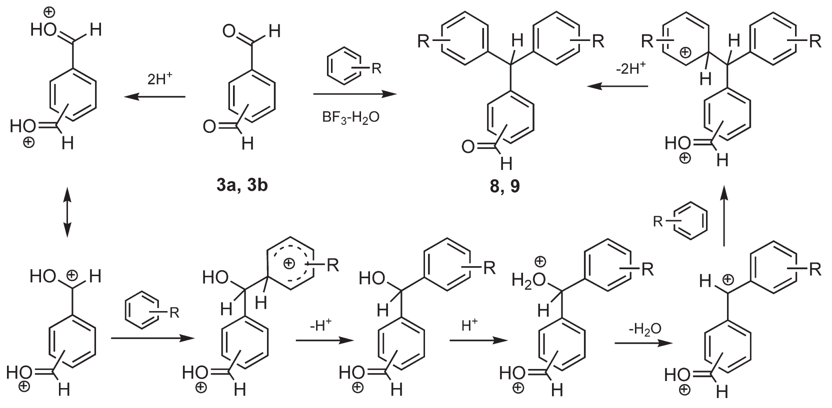
[25] Dai, W.-M.; Li, Y.; Zhang, Y.; Lai, K. W.; Wu, J. *Tetrahedron Lett.* **2004**, *45*, 1999–2001.

[26] (a) Kamata, K.; Kasai, J.; Yamaguchi, K.; Mizuno, N. *Org. Lett.* **2004**, *6*, 3577–3590. (b) Nakamichi, N.; Kawabata, H.; Hayashi, M. *J. Org. Chem.* **2003**, *68*, 8272–8273. (c) Dektar, J. L.; Hacker, N. P. *J. Org. Chem.* **1990**, *55*, 639–647. (d) Brice, L. K.; Katstra, R. D. *J. Am. Chem. Soc.* **1960**, *82*, 2669–2670.

SCHEME 7. **Reaction of Phthalic Dicarboxaldehyde with Aromatics under Superelectrophilic Conditions**



SCHEME 8. **Mechanism for the Condensation Reaction of Dicarboxaldehyde with Aromatics in BF_3-H_2O**

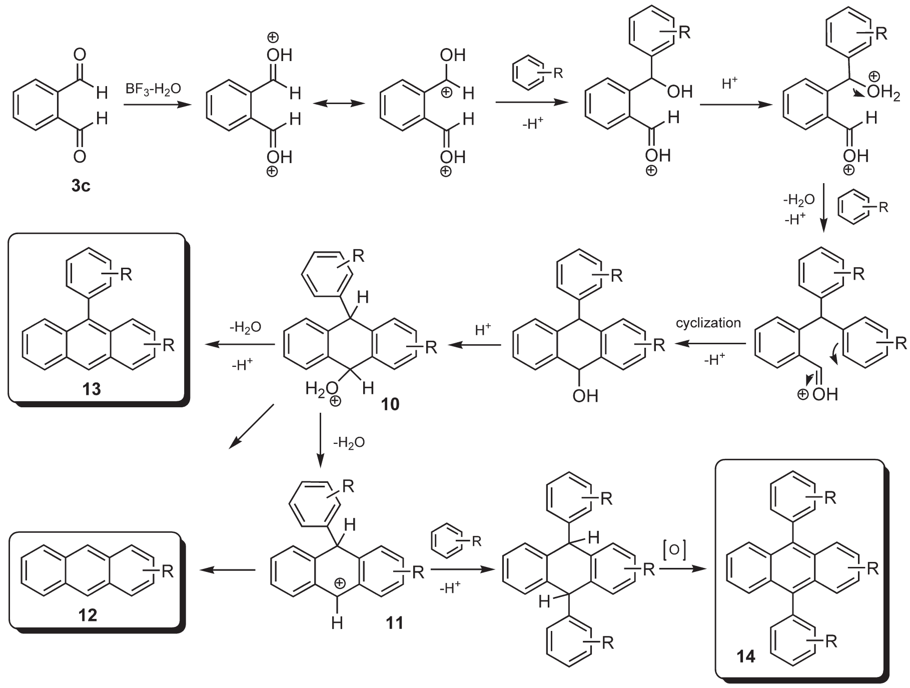


tetramethylbenzene (**1j**), 1,2,3,4-tetramethylanthracene (**12j**) was found to be the major product. With toluene, as expected, a mixture of anthracene derivatives was formed, in which 9-tolyl-2-methylanthrace (**13b**) was present in significant amount along with appreciable amount of 9,10-ditolyl-2-methylanthracene (**14b**). Similar results were also obtained with *p*-xylene (**1c**) and *m*-xylene (**1d**). One of the major difficulties associated with this methodology is in the separation of the products due to their very close R_f values in the TLC. In some cases, though the isomers were inseparable, their formation has been confirmed by GCMS and NMR analysis. Despite the problem associated with the product isolation and purification, this methodology can still offer an efficient route toward the one pot synthesis of anthracene derivatives.

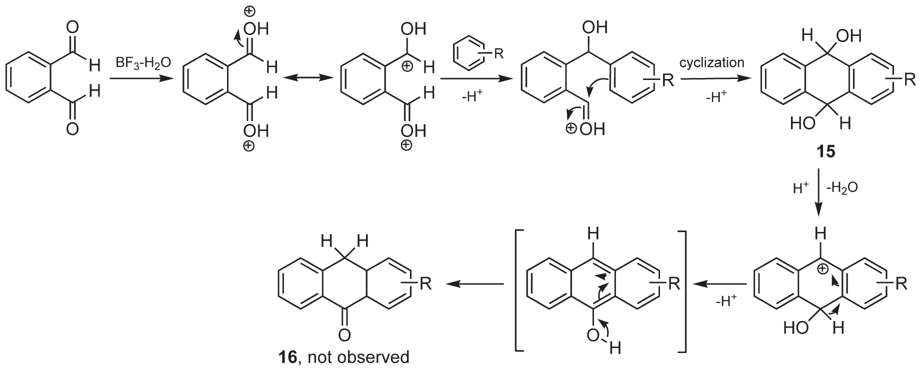
Formation of Diarylmethylbenzaldehydes. It is clear that the reaction must proceed through a diprotonated dicationic intermediate in which one of the protonated aldehyde groups is enhancing the electrophilicity of the other protonated aldehyde group through a synergic effect. Thus, as shown in Scheme 8, the reaction is clearly found to be a hydroxyalkylation to produce a secondary carbinol which undergoes further protonation followed by elimination of water to form a diphenylmethyl dication. This dicationic intermediate acts as an efficient electrophile for further reaction with aromatics to form the triarylmethane derivatives.

SCHEME 9. **Reaction of Phthalic Dicarboxaldehyde (3c) with Aromatics under Superelectrophilic Activation**

(i) Two subsequent hydroxyalkylations yielding triaryl methane followed by cyclization



(ii) Initial hydroxyalkylation yielding diaryl methanol followed by cyclization



Formation of Anthracenes. The main driving force for this reaction is the superelectrophilic activation of phthalaldehyde by BF_3-H_2O followed by its Friedel−Crafts hydroxyalkylation on the arene through the highly electrophilic protosolvated carbonyl center. In the case of isophthalaldehyde and terephthaldehyde it is found that initial hydroxyalkylation produces the corresponding diphenylmethanol and subsequently diphenylmethyl dication, which acts as an efficient electrophile for further Friedel−Crafts alkylation with aromatics to form the triarylmethane derivatives. The second aldehyde group is unaffected. However, in the case of phthaladehyde, the extreme proximity of one of the aryl ring to the second protonated aldehyde group leads to intramolecular cyclization (cycliarylation) giving rise to different anthracene derivatives (Scheme 9). If the cyclization took place after initial hydroxyalkylation step, it would follow the pathway (ii) leading to a 9,10-diol (**15**), which on aromatization (by dehydration) followed by tautomerism yields the corresponding anthrone (**16**) under the reaction conditions. However, formation of anthrone (**16**) was not found in any of these cases. This observation suggests that successive hydroxyalkylation with the arenes occurs on only one of the aldehyde groups and the greater proximity of the aryl rings with the second aldehyde group (which remains protosolvated) in the product (triarylmethane derivative) promotes intramolecular cyclization to yield anthracenes (**12**), 9-arylanthracenes (**13**), and 9,10-diarylanthracenes (**14**) through subsequent steps (pathway i). In the case of 1,2,3,4-tetramethylanthracene, due to the enhanced nucleophilicity, the strong steric effect, and the proximity, sequential hydroxyalkylation is immediately followed by cyclization and aromatization via elimination of 1,2,3,4-tetramethylphenyl cation. While BF_3-H_2O acts as a strong Brønsted acid medium, it is an effective aqueous medium also. In aqueous media, formation and stabilization of phenyl cations by hydration (highly exothermic by 51.2 kcal/mol) is known and detailed studies have been carried out in this area.[27,28] Basically the three competing pathways, (a) formation of 9-arylanthracenes **13** from **10**, (b) further Friedel−Crafts alkylation by the highly reactive diphenylmethyl cation **11** on another arene molecule and subsequent formation of 9,10-diarylanthracenes **14** by oxidation, and (c) the formation of anthracene **12** from **10** through **11**, contribute to the formation of all major products **12**, **13**, and **14**. Formation of the 9,10-diarylanthracenes (**14**) from the 9,10-dihydro derivatives could involve an oxidative dehydrogenation step in which the formation of a radical cation species[29] is suggested as an intermediate. This kind of phenomenon is common for the condensation of polynuclear aromatics under acidic conditions. One example that involves such a step is the Scholl's reaction.[30] Because 9-arylanthracenes (**13**) did not provide any 9,10-diarylanthracenes and anthracene under the reaction conditions (both in the presence and absence of aromatics), formation of anthracenes (**12**) and 9,10-diarylanthracenes (**14**) by transarylation of 9-arylanthracenes (**13**) is clearly ruled out.

Conclusions

BF_3-monohydrate is found to be an efficient and strong Brønsted acid catalyst for the hydroxyalkylation of aromatics with aldehydes. These reactions show that BF_3-H_2O can be used as a very effective protosolvating medium as well as a catalyst without the use of any additional solvent during the reaction. Diarylmethylbenzaldehydes, which can be useful synthons for various organic transformations, can be achieved easily from isoterephthalic dicarboxaldehyde and terephthalic dicarboxaldehyde using this method. Synthesis of various anthracene derivatives from phthalic dicarboxaldehyde, further adds to the importance of this method in organic synthesis. We expect wide use of less expensive BF_3-H_2O as an efficient substitute for nonoxidizing strong protic acids in a variety of acid-catalyzed organic reactions.

Experimental Section

General Procedure for the Condensation Reaction of Aldehydes/Dicarboxaldehydes with Aromatics using BF_3-H_2O as the Acid Catalyst. Aldehyde or dicarboxaldehyde (1 mmol) and neat arene (2 mL; for solid aromatics, 4 equiv) were taken in a pressure tube (30 mL). To this mixture, BF_3-H_2O (50 equiv, 4.2 g; prepared by reported procedure[6e]) was added and sealed. The mixture was stirred and heated at the required temperature under closed condition until the completion of the reaction. Progress of the reaction was monitored by TLC and GCMS. After the reaction, the reaction mixture was then poured into ice−water (10 mL) and extracted with CH_2Cl_2 (3×20 mL). Combined organic layer was washed with aq $NaHCO_3$ solution, then with brine solution, dried over anhydrous Na_2SO_4, and then solvent was removed under reduced pressure to obtain the crude product. The crude product was further purified by column chromatography over silica gel (65−250 mesh) using hexane−ethyl acetate 2−10% as eluent. Products were characterized by analyzing their spectral data (^1H, ^{13}C, ^{19}F NMR, GCMS, and HRMS data).

9-(2,5-Dimethylphenyl)-1,4-dimethylanthracene (13c). Prepared by general procedure, yield 75%. ^1H NMR δ 1.80 (s, 3H), 2.35 (s, 3H), 2.37 (s, 3H), 2.81 (s, 3H), 7.04 (s, 1H), 7.14 (s, 2H), 7.23 (dd, J = 7.78 Hz, J = 1.55 Hz, 1H), 7.27−7.32 (m, 2H), 7.38−7.42 (m, 1H), 7.44 (d, J = 8.79 Hz, 1H), 8.04 (d, J = 8.79 Hz, 1H), 8.54 (s, 1H); ^{13}C NMR δ 19.3, 19.9, 21.0, 22.2, 122.5, 123.1, 124.6, 125.3, 126.3, 128.3, 128.4, 128.8, 129.7, 129.8, 130.3, 130.7, 131.8, 134.1, 134.56, 134.63, 135.0, 135.9, 138.5; MS (EI) m/z 309.3 ($M^{\bullet+}$); HRMS (EI) m/z calcd for $C_{24}H_{22}$, 310.1722; found, 310.1719.

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Supporting Information Available: Experimental procedure, spectral data, and copies of ^1H, ^{13}C, and ^{19}F NMR spectra of the products. This material is available free of charge via the Internet at http://pubs.acs.org.

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