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BTISA-catalyzed Friedel–Crafts bimolecular cyclization of cinnamic acid under superelectrophilic solvation conditions

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ABSTRACT

Friedel–Crafts bimolecular cyclizations of cinnamic acid and cinnamoyl chloride with aromatic compounds in strong and superstrong acids in present of 1 mol% BTISA were investigated. It was demonstrated that catalytic amounts of this new superacid have essential effect on such type of reactions. Its use makes possible the preparation of indanones with quantitative yields.

1. Introduction

The use of Brønsted superacids such as TfOH, FSO_2OH and their combinations with superstrong Lewis acids (SbF_5, BF_3, $B(OTf)_3$) has received wide propagation for the preparation and study of many long-lived cationic electrophilic species (carbocations, acyl and carboxonium cations, onium ions) [1]. It should be stressed that all conceivable superacids are highly fluorinated compounds that gives reasons to consider them as an area of fluorine chemistry. Superelectrophilic solvation, as it was named by Olah and Klumpp, results in greatly enhanced electrophilic reactivity, higher reaction rates and allows to put into effect to many unusual reactions [2].

A radically new superacid—bis(trifluoromethylsulfonylimino)trifluoromethanesulfonic acid (BTISA) was synthesized [3] under the Yagupolskii principle through the replacement of the oxygen atoms of TfOH by the $=NSO_2CF_3$ group, and its acid strength ($-H_o$ is about 24) was estimated by ^{29}Si NMR spectroscopy [4]. We recently studied catalysis by the BTISA for Friedel–Crafts acylation and its advantages over other catalysts for the electrophilic acylation of aromatic substrates, such as the selectivity, small amounts (1 mol%) of the acid required, were demonstrated [5].

Friedel–Crafts bimolecular cyclizations are of our present interest in view of facts that they are more difficult to effectuate and the resulting cyclic aromatic ketones have gained widespread acceptance in the synthesis of pharmaceutical and natural products [6]. Initially we decided to study the reactivity of cinnamic acid as model substrate. Previously, this type of reactions was investigated using aluminium chloride [7], microwave-assisted/aluminium chloride [8], polyphosphoric acid [9], H-zeolites [10], and TFA/TFSA systems [11]. As far as could be determined, good yields of indanone were obtained under superelectrophilic solvation only requiring great excess of triflic acid (50–100 equiv.).

The present paper deals with cyclization of cinnamic acid and cinnamoyl chloride in strong and superstrong acids in the presence of BTISA.

2. Results and discussion

A relationship between acidity of the system, amounts of the acid and yields of reaction products (arylation, acylation and cyclization) was investigated in detail by Klumpp et al. The best yield of cyclization product (96%) was obtained in the presence of 100 equiv. of TfOH/TFA (45:55) ($-H_o$ = 11.5) at room temperature for 12 h [11b].

We studied the reaction of cinnamic acid with benzene in TFA, H_2SO_4, and TfOH in the presence of 1 mol% of BTISA (Scheme 1) under various reaction conditions. The basic data are presented in Table 1.

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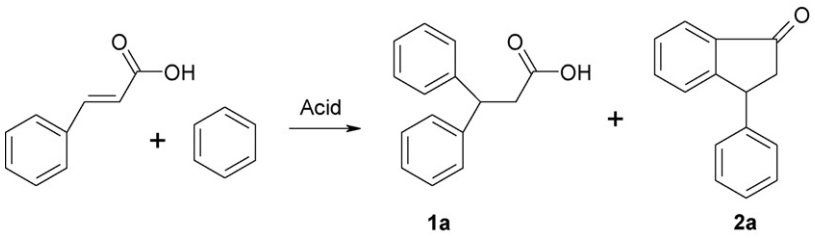
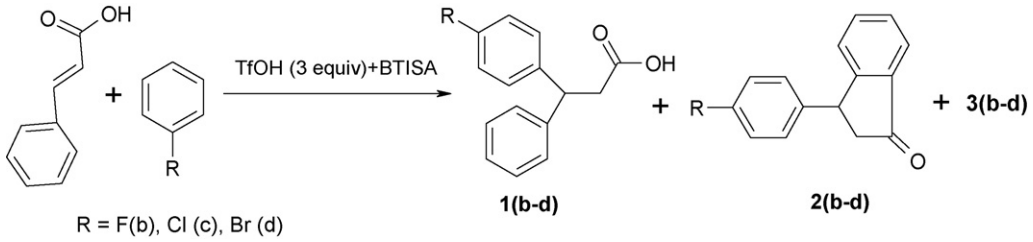


Scheme 1. Cinnamic acid interaction with benzene.

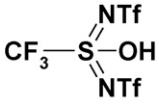
Table 1
Products and yields from the reactions of cinnamic acid with benzene in different acidic systems.

Acid (equiv) + 1% BTISA	Equivalents of benzene	τ (h)	T (°C)	Yield **1a**[a]	Yield **2a**[a]
TFA (100)	3	3	80	0	0
TFA (100)	2	18	15	0	0
H_2SO_4 (3)	3	12	15	5	0
H_2SO_4 (3)	3	17	80	76	24
H_2SO_4 (6)	6	21	80	61	39
H_2SO_4 (10)	6	21	80	100	0
TfOH (1)	3	64	70	77	23
TfOH (1)	6	19	80	67	33
TfOH (3)	3	42	15	0	100
Without BTISA [11b]					
TfOH (3)	11	12	25	47	23
TfOH (10)	11	12	25	0	88 (+9% chalcone)
TfOH/TFA 45/55 (100)	11	12	25	0	96

[a] The yields were calculated based on the ^{1}H NMR spectroscopic data.



Scheme 2. Reactions of cinnamic acid with monosubstituted benzenes.



BTISA

It becomes apparent that the addition of just 1 mol% BTISA has a significant effect on the reaction outcome: (i) 3 equiv. of TfOH are enough for quantitative yield of indanone **2a**; (ii) the reaction takes place already in H_2SO_4 (3–6 equiv.), but the arylation product **1a** was obtained preferably; (iii) the acylation product was not observed.

Since 3 equiv. of TfOH with 1 mol% BTISA turned out to be an optimum acid system, reactions of cinnamic acid with substituted benzenes have been investigated under these conditions (Scheme 2). In case of fluoro-, chloro- and bromobenzenes, we found conditions to obtain the indanones **2(b–d)** and **3(b–d)** in quantitative yields (Table 2). The isomers **2(b–d)** were formed as major products and were isolated in pure form. Their spectroscopic data and melting points agree with literature

Table 2
Products and yields of the reactions of cinnamic acid with 3 equiv. of monosubstituted benzenes in TfOH (3 equiv.) in the presence of BTISA (1 mol%).

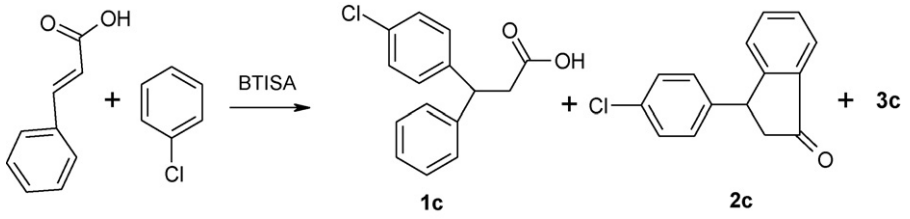
R	τ (h)	T (°C)	Yield **1**[a] (%)	Yield **2**[a] (%)	Yield **3**[a] (%)	Starting cinnamic acid (%)
F	19	16	40	15	5	40
F	96	16	35	14	4	47
F	18	106	0	78	22	0
Cl	15	15	35	14	4	47
Cl	96	25	29	53	18	0
Cl	18	130	0	86	14	0
Br	16	30	0	82	18	0

[a] The yields were calculated based on the ^{1}H NMR spectroscopic data.

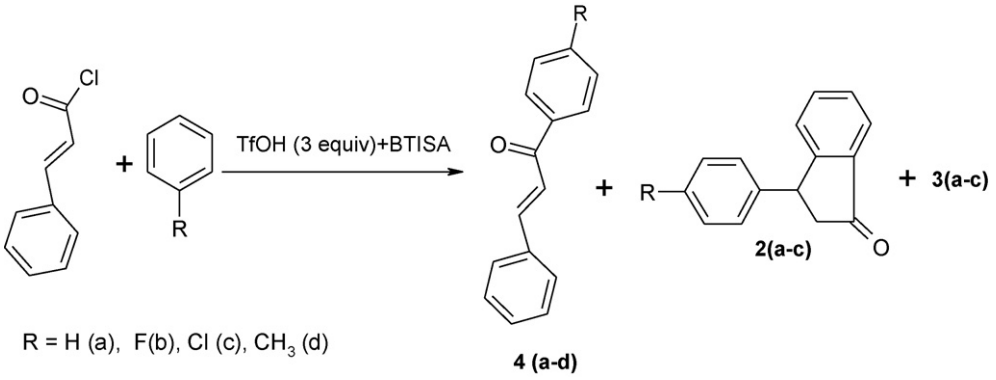
Table 3
Products and yields of the reactions of cinnamic acid with 3 equiv. of chlorobenzenes with BTISA catalysis.

BTISA (equiv.)	τ (h)	T (°C)	Yield **1c**[a] (%)	Yield **2c**[a] (%)	Yield **3c**[a] (%)	Starting cinnamic acid (%)
0.01	15	60	0	0	0	100
0.2	15	60	55	16	6	23
0.2	18	70	60	16	6	18
0.2	36	80	78	16	6	0
3	15	16	5	14	Trace	81
3	2	70	0	80	20	0

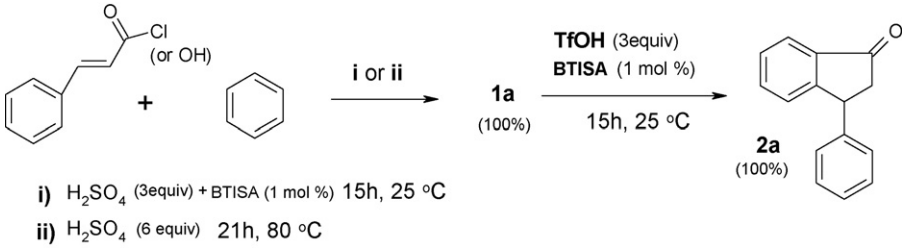
[a] The yields were calculated based on the ^{1}H NMR spectroscopic data.



Scheme 3. Reaction of cinnamic acid with chlorobenzene under BTISA catalysis.



Scheme 4. Reaction of cinnamoyl chloride with monosubstituted benzenes.



Scheme 5.

data of compounds synthesized by other methods [12]. It has not been possible to isolate isomers **3(b–d)** and to determine their structures unambiguously. A mixture of more than two indanone isomers was formed in the reaction of cinnamic acid with toluene.

In spite of encouraging findings, the study of the reaction with BTISA alone, without any added TfOH or other acid, was of fundamental importance. We investigated the reaction of cinnamic acid with 3 equiv. of chlorobenzene in the presence of different quantitative of BTISA. As shown in Table 3 1 mol% is not enough to catalyze any reaction. 20 mol% of BTISA alone is a good catalyst for the arylation reaction and 3 equiv. are sufficient to conduct the cyclization under mild conditions in a very short time with quantitative yield (Scheme 3).

Considering that BTISA is extremely hydroscopic and is used in very small amounts, it is logical to assume that its reactivity can be enhanced by using cinnamoyl chloride instead of cinnamic acid (Scheme 4). Indeed, all reactions take place at room temperature in shorter reaction time. However, the chalcone is the by-product of acylation and its yield increased with increasing electron-donor abilities of the benzenes (Table 4). So, the chalcone is the exclusive product in case of the cinnamoyl chloride reaction with toluene. We tested also the reaction with benzotrifluoride, nitrobenzene, 4-bromofluorobenzene and a mixture of cyclization products was observed in ^{1}H NMR spectra. We were not able to isolate them because of side processes like polymerization.

Based on the research performed, it may be proposed that it is advantageous to synthesize indanones in two steps: the produc-

Table 4
Products and yields of the reactions of cinnamoyl chloride with 3 equiv. of monosubstituted benzenes in TfOH (3 equiv) and BTISA (1 mol%).

R	τ (h)	T (°C)	Yield **4**[a] (%)	Yield **2**[a] (%)	Yield **3**[a] (%)
H	16	25	47	53	0
F	16	28	21	66	13
F	0.5	26	33	55	13
Cl	1	26	3	60	37
Cl	15	28	10	70	20
CH_3	15	26	100	0	

[a] The yields were calculated based on the ^{1}H NMR spectroscopic data.

tion of 3-phenylcinnamic acid (**1a**) in sulfuric acid and then its cyclization in the superacidic system (Scheme 5).

3. Conclusions

Based on the research done it may be asserted that BTISA is an excellent catalyst for use in Friedel–Crafts bimolecular cyclizations of cinnamic acid or cinnamoyl chloride with aromatic compounds. The presence of catalytic amount of BTISA under superelectrophilic solvation conditions has an appreciably influence on the reaction rate and product yields.

4. Experimental

4.1. General remarks

All reactions were carried out under a dry Ar atmosphere. Commercially available cinnamic acid was recrystallized from toluene/hexane (1:1) and dried for 6 h at 25 °C (0.1 mbar). Cinnamoyl chloride was obtained by reaction of cinnamic acid with thionyl chloride (5 mole) for 1 h at 80 °C and distilled at 50 °C (0.1 mbar). Triflic acid was distilled before use at atmospheric pressure. BTISA was prepared according to a reported procedure [3] and used as 13% solution in dry CH_2Cl_2 (P_2O_5, then CaH_2). ^{1}H and ^{19}F NMR spectra were recorded in $CDCl_3$ on Varian-GeminiVXR 300 (299.9 MHz) and Bruker 200 (188.1 MHz) spectrometers, respectively.

4.2. Reactions of cinnamic acid with benzene in different acidic systems

BTISA (11 mg, 0.027 mmol) was added to a mixture of cinnamic acid (400 mg, 2.7 mmol) and freshly distilled benzene in dry box. H_2SO_4 (98%) was added at room temperature. The mixture was heated to the desired temperature and allowed to react for a given period of time. The solution was poured onto ice and extracted with CH_2Cl_2. The extract was successively washed with water and brine than dried over $MgSO_4$ and concentrated in vacuo. The crude product was purified over silica (hexane:EtOAc, 6:1) and analyzed by NMR.

4.3. Reaction of cinnamic acid with 3 equiv. of monosustituted benzenes in TfOH (3 equiv) and BTISA (1 mol%) acidic systems

BTISA (5.7 mg, 0.01 mmol) was added to mixture of cinnamic acid (200 mg, 1.3 mmol) and freshly distilled arene (4 mmol) in dry box. Triflic acid (600 mg, 0.35 ml, 4 mmol) was slowly added at room temperature. The mixture was heated to the desired temperature and allowed to react for a given period of time. The solution was poured onto ice and extracted with $CHCl_3$. The extract was successively washed with water and brine than dried over $MgSO_4$ and concentrated on vacuo. The crude product was purified over silica (hexane:EtOAc, 6:1) and analyzed by NMR.

4.4. Reaction of cinnamoyl chloride with 3 equiv. monosustituted benzene in TfOH (3 equiv.) and BTISA (1 mol%) acidic systems

BTISA (4.9 mg, 0.01 mmol) was added to solution of cinnamoyl chloride (210 mg, 1.3 mmol) in freshly distilled arene (3.7 mmol) in dry box. Triflic acid (560 mg, 0.33 ml, 3.7 mmol) was slowly added to the stirred solution at 0 °C. The mixture was heated to room temperature and allowed to react for a given period of time. The solution was poured onto ice and extracted with CH_2Cl_2. The extract was successively washed with water, $NaHCO_3$ saturated aquatic solution and a new water, than dried over $MgSO_4$ and concentrated in vacuo. The crude product was purified over silica (hexane:EtOAc, 20:1) and analyzed by NMR.

4.5. Reaction of 3,3-diphenylpropionic acid

Triflic acid (225 mg, 0.13 ml, 1.5 mmol) was added to the stirred mixture of 3,3-diphenylpropionic acid (113 mg, 0.5 mmol) and BTISA (2 mg, 0.005 mmol) at room temperature and allowed to react for 15 h. The solution was poured onto ice and extracted with CH_2Cl_2. The extract was successively washed with water, saturated aquatic $NaHCO_3$ solution and again with water, then dried over $MgSO_4$ and concentrated in vacuo. The product was distilled. B.p. 110 °C (0.1 mbar).

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