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Multi-channel transformations of 1,3-diarylpropynones under superelectrophilic activation conditions: concurrence of intra- and intermolecular reactions. Experimental and theoretical study

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ABSTRACT

1,3-Diarypropynones undergo concurrent multi-channel transformations in Bronsted (FSO_3H, TfOH) and Bronsted–Lewis (HF–SbF_5, TfOH-SbF_5) superacids, leading intramolecularly to 3-arylindenones, or intermolecularly to 1,3,3-triarylpropenones, and dimeric structures. The outcome depends on the electronic donor-acceptor properties of the substituents in the aromatic rings of the 1,3-diarylpropynones, and on the added aromatic external π-nucleophiles. The orbital energies, atom charges, orbital contributions, and global electrophilicity indices of the cationic intermediates have been calculated by DFT methods to explain these transformations.

1. Introduction

Superelectrophilic activation of organic compounds by Bronsted or Lewis superacids is an effective method of organic synthesis.[1,2] Exploration of this approach to the chemistry of acetylenes allows the synthesis of many valuable compounds: carbo- and heterocycles, vinyl triflates (sulfonates, fluorides), products of triple bond hydroarylation, etc.[3]

In our previous studies,[4–8] we have shown that 1,3-diarylpropynones may be involved in various reactions in Bronsted [FSO_3H, CF_3SO_3H (TfOH)], and conjugated Bronsted–Lewis (HF–SbF_5, TfOH–SbF_5) superacids. The first protonation of the propynone system of compound **1** occurs at the carbonyl oxygen, leading to unreactive cation **A** (Scheme 1), which were thoroughly characterized by NMR methods.[5,6] Further protonation at the α-carbon atom of the triple bond results in the formation of highly reactive superelectrophilic dication **B**. The latter may react in three different pathways: intramolecular cyclization into 3-arylindenones **2** (path *a*),[4–7] intermolecular formation of triple bond hydroarylation products **3** in the presence of arenes (path *b*), and by interaction with the O-protonated form of **A**, leading to dimeric compounds **4** (path *c*).[8]

This synthetic method gives access to 3-arylindenones **2**, which have found applications in medicinal chemistry,[9–14] and to the difficultly available 1,3,3-triarylpropenones **3**, **4**.

In this paper we analyze the multi-channel transformations of 1,3-diarylpropynones **1**, under the superelectrophilic activation conditions of Bronsted superacids. The main goal of this work is the investigation of the influence of electronic donor–acceptor properties of the substituents R and R′ in the aromatic rings of compounds **1** on their concurrent transformations. Structural tuning by changing the substituents R, R′ allows us to achieve selectivity in the reaction pathways of intermediates **B**, as is shown in Scheme 1. Both experimental and theoretical computational studies have been carried out to elucidate this problem.

2. Results and discussion

2.1. Experimental study

In our previous work,[4–6] it has been shown that in various superacidic systems (FSO_3H, TfOH, HF–SbF_5, TfOH–SbF_5) 1,3-

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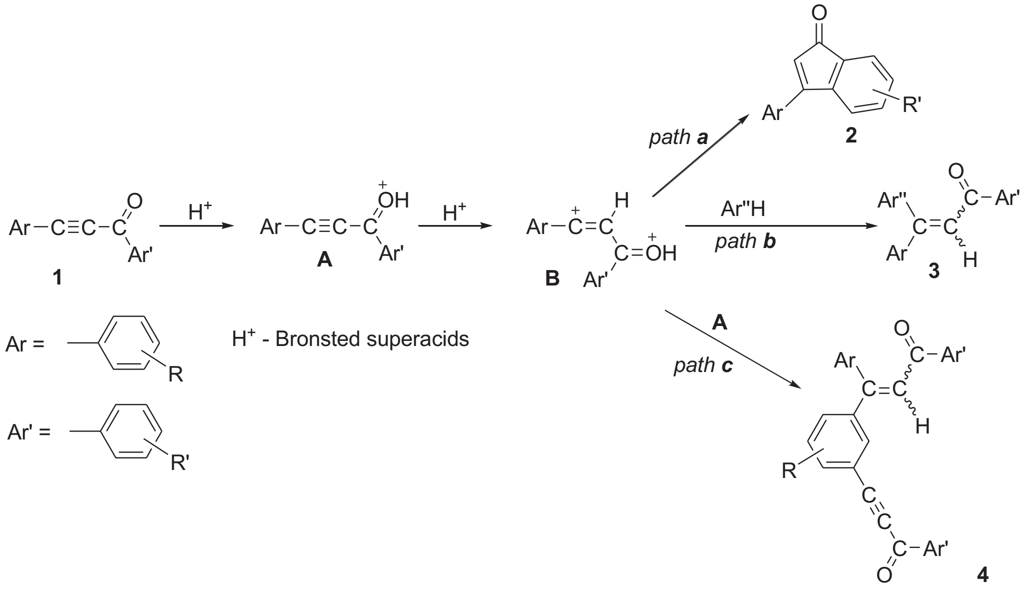
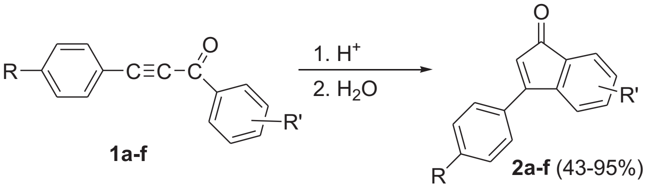


Scheme 1.

diarylpropynones **1a**–**f**, bearing substituents R=H, 4-Me, 4-MeO in the arene ring, conjugated with an acetylene bond, intramolecularly give 3-arylindenones **2a**–**f** (Scheme 2).



1: R = R' = H (a); R = 4-Me, R' = H (b);
R = MeO, R' = H (c), 3-MeO (d), 3,4-Me_2 (e);
R = H, R' = 3-MeO (f)

2: R = R' = H (a); R = Me, R' = H (b);
R = MeO, R' = H (c), 6-MeO (d), 5,6-Me2 (e);
R = H, R' = 6-MeO (f)

Scheme 2.

The presence of two or three methyl groups in the aromatic ring conjugated with the triple bond in propynones **1g**,**h** (Scheme 3) change dramatically their reaction pathway, leading to dimers **4a**,**b** in FSO_3H at -50 to -20 °C in 0.5 h.[8] This reveals that for compounds **1g**,**h**, the intermediate dications **B** react intermolecularly with more nucleophilic arene rings of the cations **A** (path *c* in Scheme 1), rather than undergo intramolecular cyclization into 3-arylindenones (path *a* in Scheme 1).

Further methyl substitution in compound **1i** results in the formation of oligomers in TfOH (Scheme 4), due to electrophilic reactions, involving the available positions in the pentasubstituted arene ring.

Having no available position for electrophilic substitution in the same arene ring, pentamethyl ketone **1j** gives again indenone **2g**.

Another structural variation in the 1,3-diarylpropynones is the changing of substituent R′ in the aromatic ring, conjugated with the carbonyl group. For compounds **1a**–**f**, where R′=H, 3-MeO, 3,4-Me_2, cyclization into indenones **2a**–**f** takes place (Scheme 2). In compound **1k** with substituent R′=4-MeO, despite its electron-donor character, no cyclization occurs, only oligomers are formed (Scheme 6). The corresponding intermediate cation **B** does not intramolecularly attack the Ar′CO ring in the *meta*-position to the methoxy group.

Formation of the dimers **4a**,**b** (Scheme 3), reveals that cations **B** may react with arenes (path *b* in Scheme 1). The next step in our study was the investigation of reactions of 1,3-diarylpropynones **1** with benzene derivatives. Indeed, cations **B** reacted with arenes, forming 1,3,3-triarylprop-2-en-1-ones **3**. The data obtained are given in Table 1.

The exact *E*-/*Z*-configuration of 1,3,3-triarylpropenones **3a**–**j** (Table 1) was determined by X-ray analysis (for compounds *Z*-**3e**, *Z*-**3f**, and *Z*-**3j**, Fig. 1) and by ^1H NMR spectroscopy. The reference signal, used for stereochemical assignment of *E*-/*Z*-configuration, was the resonance of the vinyl proton at the double bond >C=CH–. The signal of the vinyl protons of *E*-isomers is observed mostly up-field, and that of *Z*-isomers down-field, as was previously described for related structures.[8,15–17]

According to the X-ray data, the bond lengths and angles in compounds *Z*-**3e**, *Z*-**3f**, and *Z*-**3j** are typical. It should be noted that compound *Z*-**3e** contains two independent molecules in an asymmetric unit, which have a different conformation. The dihedral angle between six-membered arene fragments (Fig. 1a) in the first molecule of *Z*-**3e** is 13.5°, whereas the analogous angle in the other molecule is 63.1°.

We investigated the reaction of propynones **1a**–**k** with benzene, and some its derivatives. Amazingly, compounds **1a**–**f** do not react at all with arenes, even with good π-donors such as anisole, veratrole, and *meta*-xylene. They give exclusively the intermolecular