

Supplementary Material

Highly Efficient Carbene and Polycarbene Catalysis of the Transesterification Reaction

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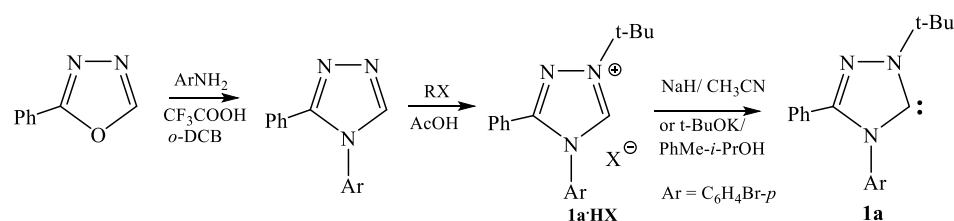
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1. Methods for the preparation of carbenes and precarbenes used in the work

The azolium salts **1a,b** · HX and the bisazolium **7** · 2HX salt (X = Br, ClO₄) were each synthesized via a three-stage method. Initially, the desired 1,2,4-triazoles were produced by the ring transformation of 2-phenyl-1,3,4-oxadiazole or *p*-phenylene-2,2'-bis-1,3,4-oxadiazole using amines. The requisite triazolium salts were prepared by quaternization of the newly formed triazoles with *tert*-butyl iodide or *p*-bromobenzyl bromide [12–15] (Scheme 1).

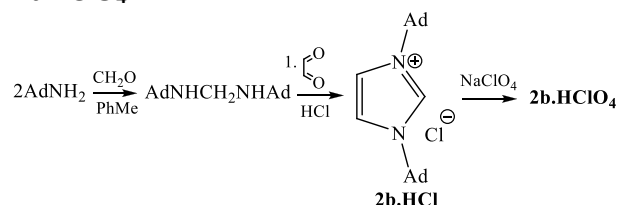


Scheme 1. Synthesis of 1,2,4-triazol-5-ylidene **1a [12–15]**

The individual carbenes **1a** and **7** were produced by deprotonation of the appropriate salts with potassium *tert*-butoxide in a mixture of toluene and isopropanol or by the reaction with sodium hydride in acetonitrile (shown in Scheme 1 on the instance of **1a**).

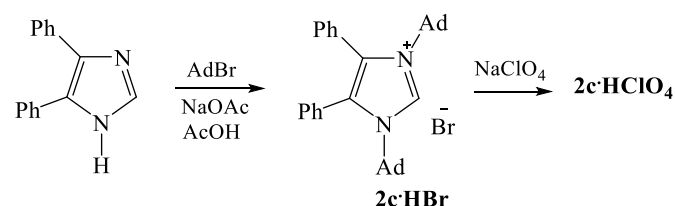
Compounds **2a**·HX and **3a,b**·HX were synthesized by alkylation of imidazole or benzimidazole with benzyl chloride or dimethyl sulfate in the presence of sodium acetate in acetic acid.

Salt **2b·HCl** was obtained using the procedure developed by Arduengo [16-18]. This procedure involved the reaction of 1-aminoadamantane with formaldehyde in toluene solution, followed by subsequent interaction of the condensation product with aqueous glyoxal in the presence of hydrochloric acid (Scheme 2). Further replacement of the chloride anion was carried out using sodium perchlorate in an aqueous medium to form the salt **2b·HClO₄**.



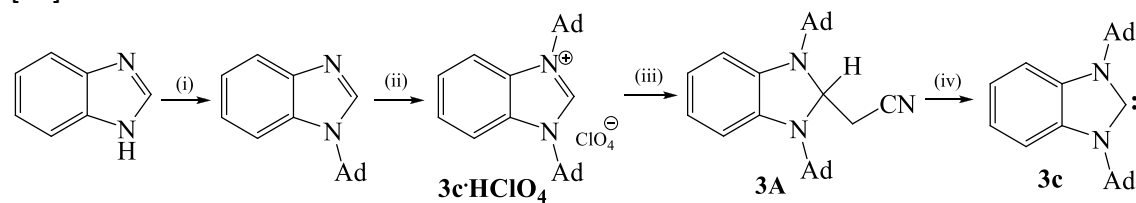
Scheme 2. Synthesis of imidazolium salt 2b·HClO₄ [16-18]

Compound **2c·HX** was synthesized by alkylation of 4,5-diphenylimidazole with 1-bromoadamantane in acetic acid [19] (Scheme 3).



Scheme 3. Synthesis of imidazolium salt 2c [19].

Salt **3c·HX** was prepared by quaternization of 1-adamantylbenzimidazole with 1-bromoadamantane in *o*-dichlorobenzene in accordance with the methods described in publications [20-22] (Scheme 4). Initial 1-adamantylbenzimidazole was obtained by alkylation of benzimidazole with 1-bromoadamantane in the presence of K_2CO_3 in *o*-dichlorobenzene [21].

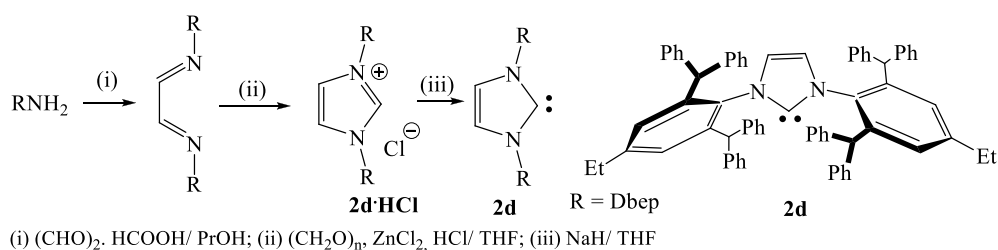


(i) AdBr, K_2CO_3 , *o*-DCB; (ii) 1. AdBr, *o*-DCB. 2. NaClO₄; (iii) NaH, CH₃CN; (iv) 180 °C, - CH₃CN

Scheme 4. Synthesis of 1,3-di(1-adamantyl)benzimidazol-2-ylidene 3c and its precarbene 3c·HClO₄ [20-22].

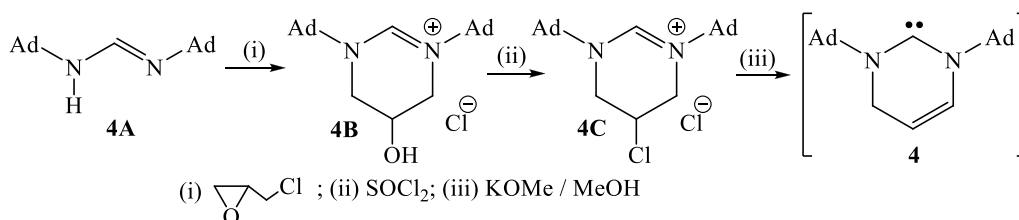
Salt **2d·HX** was prepared by treatment of 2,6-dibenzhydryl-4-ethylaniline with glyoxal in propanol in the presence of formic acid, followed by further cyclization of the isolated glyoxaldiimine with paraformaldehyde in chloroform in the presence of zinc chloride and hydrochloric acid [23] (Scheme 5).

The individual carbenes **3c** and **2d** were synthesized from the corresponding salts via the reactions with sodium hydride in acetonitrile and THF, respectively [20,22,23] (Schemes 4,5). In the first case, the cyanomethyl derivative of 2H-benzimidazole **3A** was formed initially and decomposed in the solid state at 180 °C in vacuo (Scheme 4).

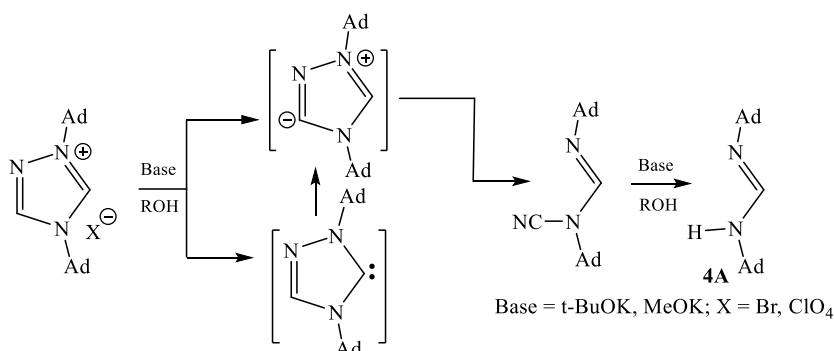


Scheme 5. Synthesis of imidazol-2-ylidene 2d [23].

Carbene **4** was generated from the appropriate salt **4C** (Scheme 6). The latter compound was synthesized in four distinct stages [19, 24]. Initially, 1,3-di(1-adamantyl)formamidine **4A** was produced via reaction of the 1,4-diadamantyl-1,2,4-triazolium salt with alkoxides (Scheme 7). The interaction of the amidine **4A** in the presence of an excess of epichlorohydrin resulted in the formation of the 1,3-di(1-adamantyl)-5-hydroxy-5,6-dihydro-4H-pyrimidinium salt **4B**. Subsequent chlorination of the latter compound with thionyl chloride afforded the 5-chlorosubstituted salt **4C**. The dehydrochlorination of 1,3-di(1-adamantyl)-5-chloro-5,6-dihydro-4H-pyrimidinium chloride **4C** was carried out by reaction with sodium hydride thereby generating carbene **4** (Scheme 6) [19, 24].

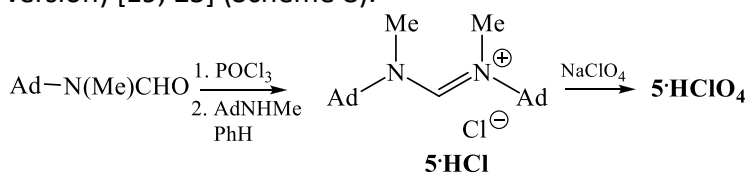


Scheme 6. Generation of carbene 4 [19, 24].



Scheme 7. Synthesis of 1,3-di(1-adamantyl)formamidine 4A [19].

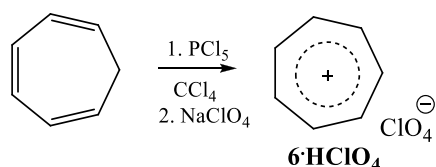
The precarbene **5·HX** was synthesized via reaction of *N*-methyl-*N*-(1-adamantyl)formamide with phosphorus chloroxide in benzene solution, followed by reaction with methyl-(1-adamantyl)amine according to the modified Vilsmeier-Haack method (the Bredereck's version) [19, 25] (Scheme 8).



Scheme 8. Synthesis of 1,3-di(1-adamantyl)-1,3-dimethylformamidine salt $5 \cdot \text{HClO}_4$ [19, 25]

The structures of the carbenes **1a**, **2d**, **3c**, **5**, **7** were confirmed on the basis of single crystal X-ray diffraction studies [12, 15, 22, 23, 25].

The precarbene tropylium perchlorate **6**·HClO₄ was produced by chlorination of cycloheptatriene with phosphorus pentachloride in a carbon tetrachloride solution [26] (Scheme 9).



Scheme 9. Synthesis of tropylium perchlorate $6 \cdot \text{HClO}_4$ [26]

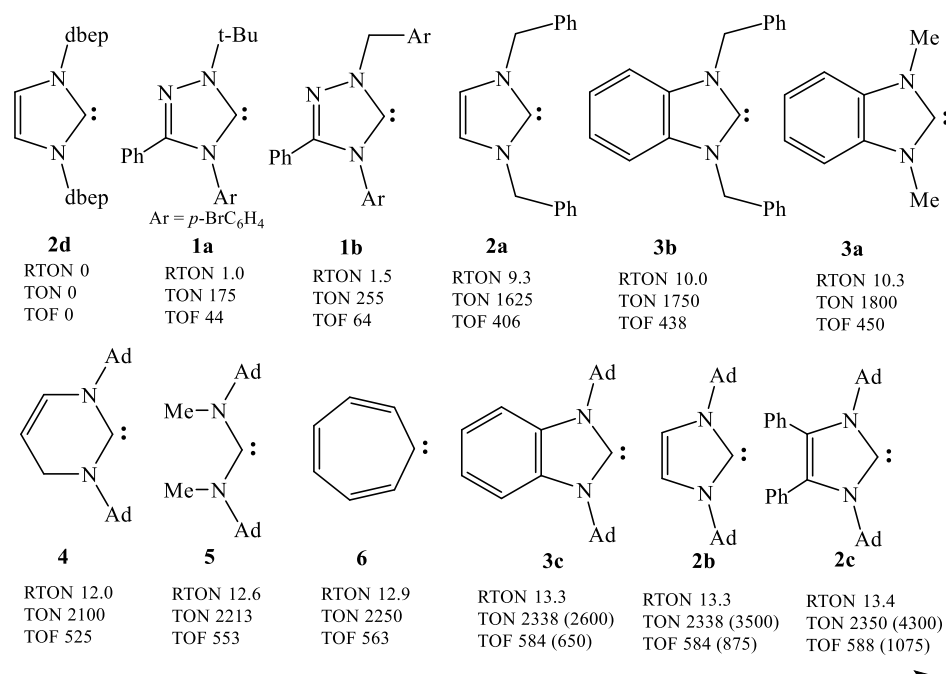
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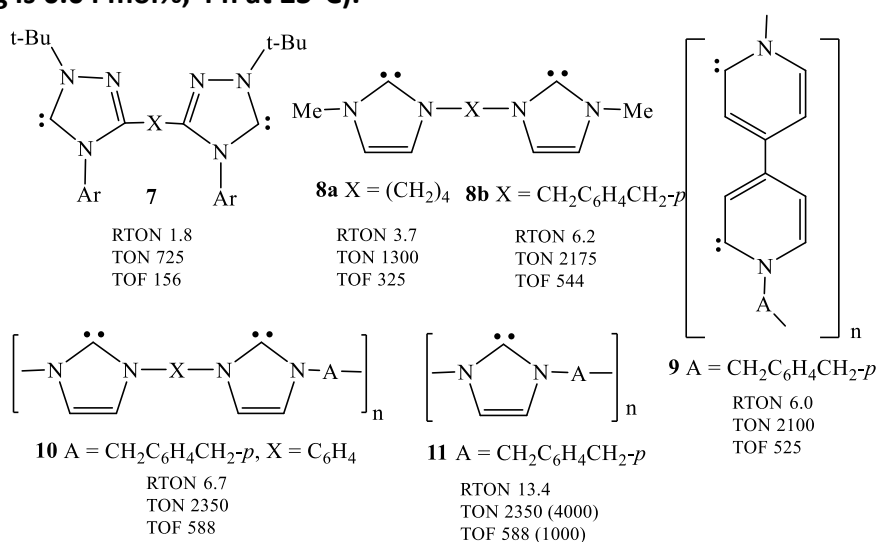
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2. The efficiency series for carbene catalysts in the transesterification reaction of ethyl benzoate in methanol

2.1. The efficiency series for monocarbene catalysts in the transesterification reaction of ethyl benzoate in methanol (the molar ratio of the reactants is 1:9, the catalyst loading is 0.04 mol%, 4 h at 23°C; the compounds are disposed here and further in order of increasing catalytic efficiency)



2.2. The efficiency series for bis- and polycarbene catalysts in the transesterification reaction of ethyl benzoate in methanol (the molar ratio of the reactants is 1:9, the catalyst loading is 0.04 mol%, 4 h at 23°C).



The data in brackets are presented for the most active catalysts **2b,c,3c,11** at the ratio 1:18, the catalyst loading is 0.01 mol%, 4h at 23°C