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The reactions of 3,7-dimethylenebicyclo[3.3.1]nonane, norbornadiene and *cis*,*cis*-1,5-cyclooctadiene with pentafluoro-λ^6-sulfanyl chloride

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ABSTRACT

Radical transannular cyclizations of the non-conjugated dienes, such as 3,7-dimethylenebicyclo[3.3.1]-nonane and norbornadiene with SF_5Cl upon UV-irradiation led to the corresponding SF_5-substituted 3,7-noradamantane and nortricyclanes with high yields. Radical reaction of *cis*,*cis*-1,5-cyclooctadiene with SF_5Cl led to a product of SF_5Cl addition to one of the diene double bonds either UV-irradiation or triethylborane were used for radical initiation.

1. Introduction

Introduction of a SF_5 group into organic compounds has been known for over 50 years ago, but the number of SF_5-containing compounds is limited by SF_5 sources or building blocks. Compounds containing SF_5 group possess unique properties due to the low surface energy, high chemical resistance, thermal stability, high electronegativity and lipophilicity [1–6]. These properties could lead to potential biological activity of SF_5-based compounds. A number of patents describe the properties of SF_5-derivatives as fungicides, herbicides and insecticides [4,7,8]. An SF_5 analogue of the insecticide Fipronil [9] has a significantly higher activity than the corresponding CF_3 compound.

Important and convenient methods for the addition of the SF_5 group into organic compounds are based on radical addition of SF_5Cl to unsaturated substrates using thermolysis [10], UV-irradiation [5] and $(CH_3CH_2)_3B$ as a low-temperature initiator [11–12]. The prepared addition products are widely used for the synthesis of various classes of SF_5-based compounds (alcohols, aldehydes, ketones, acids, aromatic, alkenes, acetylenes, heterocycles); but only a relatively few SF_5-carbocycle compounds with norbornane cage have been synthesized [5,13].

Among the alkenes, the non-conjugated polyenes are of special interest because their transformations lead to various biologically active polycyclic compounds [14,15]. Polycycles with adamantyl and noradamantyl moieties are often used as building blocks for new drugs with various types of physiological activity [16–19]. Derivatives including nortricyclane and norbornane bridged cycles are structurally similar to natural terpenes. A number of such polycycles show activities for the treatment or the prevention of neurologic diseases [20–23].

Convenient and selective preparations of functional derivatives of adamantane and noradamantane are based on transannular cyclizations of bicyclo[3.3.1]nonane dienes with electrophilic [24–28] or radical agents [29–31]. The transannular cyclizations of norbornadiene with electrophilic and radical reagents [32–36] are used for selective preparation of nortricyclane derivatives. In contrast to norbornadiene reactions, the selectivity of *cis*,*cis*-1,5-cyclooctadiene reactions and structure of the formed products depend strongly on the nature of the reagents, solvents and the presence of catalysts or initiators [35–39]. Products of the addition to one double bond along with the cyclization products to bicyclo[3.3.0]octane derivatives are characteristic for radical reactions of *cis*,*cis*-1,5-cyclooctadiene [35–38].

To the best of our knowledge no reactions of non-conjugated dienes with SF_5Hlg (Hlg = Cl, Br) leading to cyclization products have been reported. The purpose of this work was to examine the

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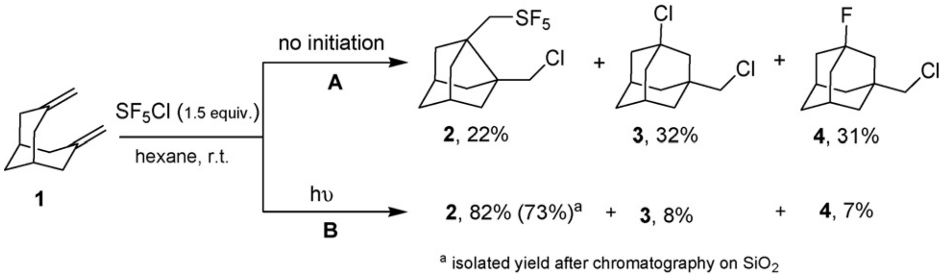


Scheme 1. The yields were determined by NMR and GS–MS.

effectiveness of electrophilic SF_5 radicals in reactions of non-conjugated dienes with different cyclization possibilities, such as 3,7-dimethylenebicyclo[3.3.1]nonane, norbornadiene and *cis*,*cis*-1,5-cyclooctadiene.

2. Results and discussion

2.1. Transannular cyclization 3,7-dimethylenebicyclo[3.3.1]nonane with SF_5Cl

Cyclization of 3,7-dimethylenebicyclo[3.3.1]nonane (**1**) with SF_5Cl in dry *n*-hexane proceeded for 3 h at ambient temperature without any special initiation and gave a mixture of three products **2**–**4**, in similar yields: the desired SF_5-substituted noradamantane **2** and two adamantane derivatives, **3** as Cl_2 addition product and **4** as a “Cl–F” addition product (Scheme 1, path **A**).

The ^1H NMR spectrum of product **2** shows two characteristic signals, a singlet of the CH_2Cl group at 3.55 ppm and a pentet for the CH_2SF_5 group at 3.94 ppm (J = 9.0 Hz). In the ^{19}F NMR spectrum of **2** the typical appearance of the AB_4-spin system for the SF_5-substituent was observed with nine lines for the apical fluorine atom (A-part) at 85.1 ppm and a doublet of multiplets of the basal fluorines (B_4-part) at 69.4 ppm (J = 143.0 Hz). The characteristic signals of adamantanes **3** and **4** in NMR spectra {^1H NMR: **3** (s, 3.28 ppm CH_2Cl), **4** (s, 3.32 ppm CH_2Cl) and ^{19}F NMR **4** (s, −133.8 ppm the fluorine atom in the bridgehead position)} are in agreement with those reported for **3** [40] and **4** [28].

It has been previously shown, that transannular cyclization of bicyclo[3.3.1]nonane dienes with radical agents (CCl_4/AIBN [29], C_6H_5SH, CH_3PhSO_2Hlg (Hlg = Cl, Br) [30]) and with polyfluoroalkyl radicals [31] gives mainly noradamantane derivatives. Using the DFT method, we have established that formation of noradamantane derivatives at cyclization of diene **1** with electrophilic trifluoromethyl radical corresponds to kinetic control [31]. This allowed us to assign of noradamantane product **2** forming through the radical mechanism. We consider, that formation of radicals without special initiation of reaction diene **1** with SF_5Cl (Scheme 1, pathway A), proceeds through the reagents interaction in accordance to olefin-induced homolysis [41]. The latter can be proved by a considerable increased yield of the SF_5-product **2** by carrying out the reaction of **1** with SF_5Cl upon irradiation with a Hg lamp in quartz apparatus (Scheme 1, path **B** and Fig. 1).

The formation of products **3** and **4** with the adamantane framework points to a polar mechanism of the electrophilic transannular cyclization of diene **1** with molecular chlorine and “F–Cl” accordingly (Fig. 1). This mechanism is well known for many Ad_E reactions of bicyclo[3.3.1]nonane dienes with electrophilic agents [24–28]. We suppose, that molecular chlorine was formed by recombination of chlorine atoms or reaction of $Cl^{\bullet}$ and SF_5Cl. Participation of the molecular chlorine in the formation of product **3** is confirmed by the data from paper [42], in which dichloride **3** was obtained by dry chlorine passing through a solution of diene **1** in CCl_4. In contrary, cyclization of diene **1** with a chlorine atom and a $^{\bullet}CCl_3$ radical obtained by homolysis of CCl_4 with AIBN [29] gives mostly a chloronoradamantane derivative as the major product. The formation of “F–Cl” addition products in reactions of SF_5Cl [10] with olefins has been well known. This is supported by DFT computation that showed that the SF_5Cl molecule dissociates easier to the interhalogen FCl and SF_4 than to the radical products $^{\bullet}SF_5$ and $Cl^{\bullet}$ or $^{\bullet}SF_4Cl$ and $F^{\bullet}$ [43].

So, carrying out the reaction of **1** with SF_5Cl upon UV-irradiation (Scheme 1, way **B**) is an effective route for increasing the yield of product **2**, and for decreasing the yields of **3** and **4** in the electrophilic reactions.

2.2. The transannular cyclization of norbornadiene with SF_5Cl

Norbornadiene **5** and SF_5Cl upon irradiation with a Hg lamp in quartz apparatus led to formation of cyclization products **6** and **7** in high yields (Scheme 2).

Products of the “F–Cl” addition were not observed in the ^{19}F NMR spectra. Nortricyclane **6** was separated from the reaction mixtures by silica gel column chromatography. The formation of the product **7** was confirmed by ^1H and ^{19}F NMR spectra. It is well known from the literature that proton signals H–C^5 for *endo*-3-halogen,*exo*-5 substituted nortricyclanes are downfield shifted relative to H–C^5 signals of *exo*-3-halogen,*exo*-5 isomers [33,35,36]. In the ^1H NMR spectrum of **7** the pentet of the H–C^5 proton signal (4.54 ppm, J = 8 Hz) is downfield shifted relative to H–C^5 proton signal of **6** (3.81 ppm, J = 8 Hz). Moreover, the ^1H NMR spectra of product **6** and **7** show the characteristic singlets of the C^3HCl group protons, at 3.88 and 3.99 ppm respectively. In the ^{19}F NMR spectra of **6** and **7** the typical appearance of the AB_4-spin system for the

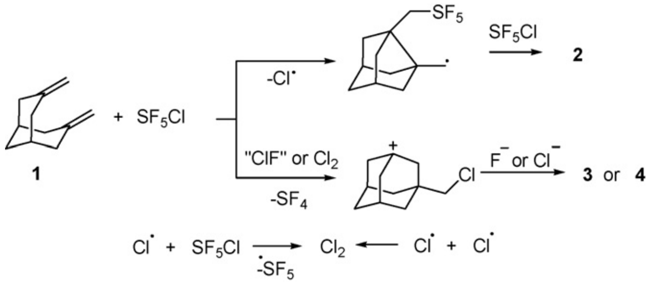
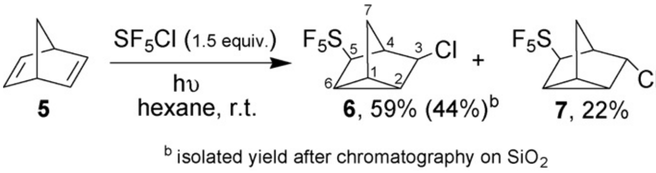


Fig. 1. The cyclization mechanism of 3,7-dimethylene[3.3.1]nonane (**1**) with SF_5Cl without initiation.



Scheme 2. The yields were determined by NMR and GS–MS.