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Synthesis and rearrangement reactions of 1,4-dihydrospiro[1,4-methanonaphthalene-9,1′-cyclopropane] derivatives

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ABSTRACT

Reactions of benzyne with ester derivatives of spiro[2.4]hepta-4,6-dien-1-ylmethanol were performed. By rearrangement reaction of cyclopropyl methanol units of ((1s*,1′R*,2R*,4′S*)-1′,4′-dihydrospiro[cyclopropane-1,9'-[1,4]methanonaphthalen]-2-yl) methyl 3,5-dinitrobenzoate (**13**) and its isomer (**14**), corresponding allyl chlorides were obtained. Two rearrangement products were obtained from bromination of compound **13** with an equivalent amount of Br_2. A naphthalene derivative including allyl and CHO moiety was formed for reactions from compounds with epoxide of **13** and **14** with NaN_3 by sequential rearrangements. Formations of products are discussed.

1. Introduction

Among the molecular rearrangements in organic chemistry, Wagner-Meerwein rearrangement takes an important place [1]. This rearrangement can be seen in the form of single or sequential rearrangements, and they can lead to the formation of important structures. Transformation of cyclopropylmethanols and their derivatives into homoallylic derivatives is a useful reaction [2].

In compounds **1** and **2**, a cyclopropane ring is combined with benzonorbornadiene and benzobarrelene giving skeletal rearrangements [1b,3] in ionic medium. When R was CH_2OH in **1** and **2**, we observed that their reactions with $SOCl_2$ gave sequential rearrangements starting with cyclopropane rings [4]. Furthermore, we observed that the reaction of **2** (R = COOMe) with Br_2 gave products derived from skeletal rearrangements (Fig. 1) [5]. Starting from the compound **1** where R (COOMe) is *exo*-configuration, the same route was used in the synthesis of *exo*-9-ethyl-1,4-dihydro-1,4-methanonaphthalene [4b,6].

To form a substituted cyclohexene derivative, Diels—Alder reaction is realized stereospecifically between a conjugated diene and a dienophile. The Diels—Alder reactions are particularly used in synthetic organic chemistry, and their reaction product is called adduct [7]. Adducts **4** were synthesized from the reactions of compound **3** with different dienophiles, and their rearrangement reactions were investigated [8]. Recently, we reported that rearrangements of adduct **5** and adduct of compound **6** with dimethyl 1,2,4,5-tetrazine-3,6-dicarboxylate rearranged without $SOCl_2$ (Fig. 1) [9]. These rearrangements are new and also include cleavages of carbon-nitrogen or carbon-carbon bonds in them [9].

Benzyne is used in the Diels-Alder reactions as dienophile [10]. It is used in the synthesis of cyclopropanetad benzonorbornadiene and benzobarrelene derivatives **1** and **2** as dienophile [1b,4]. Adducts of compound **3** and its derivatives with benzyne are important because interesting rearrangements may occur in them. Therefore, adducts of **3** and its ester derivatives with benzyne were synthesized, and investigated their rearrangements reactions.

2. Results and discussion

Spiro alcohol **3** and its ester derivatives **7**—**9** were synthesized by a known method [9a]. Benzyne is a good dienophile and is formed in the reaction medium as an intermediate product. The reaction medium is acidic because benzenediazonium 2-

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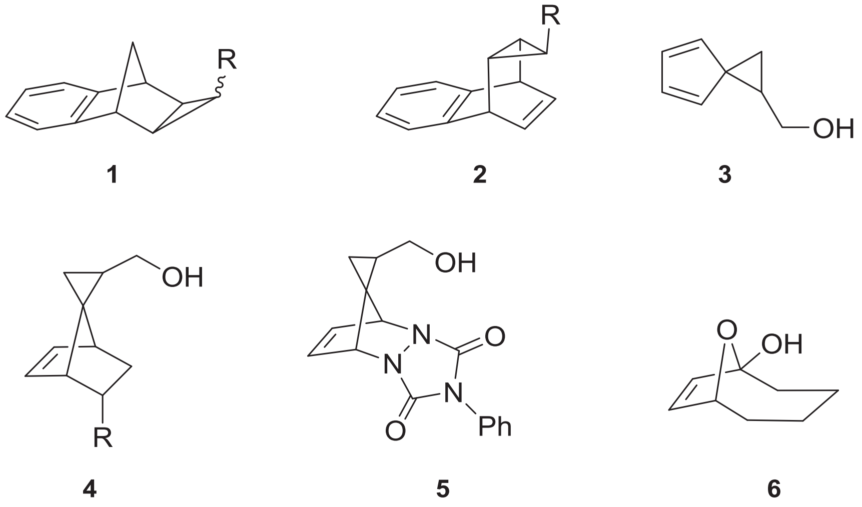


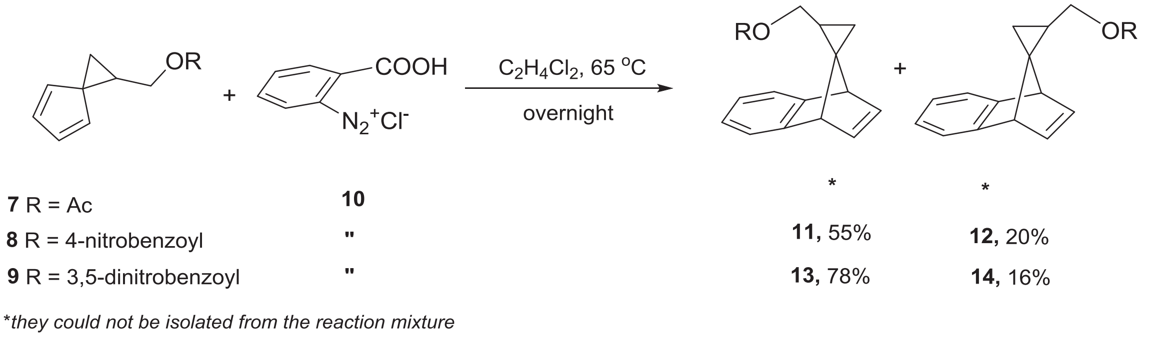
Fig. 1. Structures of compounds having tendency to rearrangement.

carboxylate hydrochloride salt (BDCHCl) was used as the source of the benzyne [10,11]. Spiro alcohol **3** was not used because it might be unstable in the related reaction condition.

The reaction of ester **7** whose R group is Ac with BDCHCl (**10**) was performed. The ^{1}H NMR spectrum of its reaction mixture was investigated and some peaks belonging to two isomeric adducts were determined. However, no adduct could be purified from this reaction mixture by chromatographic methods. The reaction of ester **8** with **10** was also performed in the same way. By carefully repeated column and thin layer chromatography, two products were isolated from their reaction (Scheme 1). Because approach of the benzyne to ester **8** is from two directions, these products should be isomeric adducts **11** and **12** as *exo*- and *endo*-products in the reaction of a diene such as **8**. The lack of isolation of the isomeric products formed in the reaction of **7** with benzyne should be due to their physical properties. The larger the group of isomeric adducts, the more their physical properties are different. The mass and volume of acetyl group is less than that of 4-nitrobenzoyl group. Probably, a molecule with R unit such as the 3,5-dinitrobenzoyl compared to the 4-nitrobenzoyl group will be more polar. Therefore, isomeric adducts may be isolated easily. Moreover, we observed similar properties in the reactions of **7**–**9** with phenyltriazolinedione (PTAD) [9a]. Therefore, two isomeric adducts **13** and **14** were obtained in pure from the reaction of ester **9** with **10** in the same condition. Their structures were determined from NMR spectra; especially NOE (Nuclear Overhauser Enhancement) measurements played an important role by determination of the correct structures. To be sure about the exact configurations of the isomeric adducts, X-ray analysis of the main product was performed. After determination of the correct structure of the isomer **13**, we assigned the isomeric structure to the compound **14** (Fig. 2). When the reactions of ester **9** with **10** and ester **8** with PTAD[9a] were considered, the structure of major isomer formed in the reaction of **8** with **10** may be that of compound **11** (Scheme 1).

X-ray diffraction analysis confirmed the structure of **13** (Fig. 2). The compound crystallizes in the triclinic space group P-1 with one isolated molecule in the asymmetric unit. C-C (cyclopropane) distances are in the range of 1.520(3)-1.484(3) Å. The structure contains three asymmetric carbon atoms and stereogenic centers are as follows: C5(S), C8(R), and C13(R).

Adducts **11**–**14** are benzonorbornadiene derivatives including a spirocyclopropane ring. The compounds **11**–**14** have now suitable functional groups that have great tendency for rearrangement [4,5]. To study the tendency for the skeletal rearrangement, the



Scheme 1. Cycloaddition reactions of benzyne with ester **7**–**9**.