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Studies on synthesis and photoreaction of tricycloundecanes endowed with β,γ-enone chromophore: Towards angular triquinanes and annulated bicyclo[4.2.0]octanes

Raghaba Sahu, Vishwakarma Singh*

Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai 400 076, India

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ABSTRACT

Cycloaddition of annulated cyclohexa-2,4-dienone with electron deficient π-partners leading to tricycloundecanes having a β,γ-enone chromophore has been reported. Studies on the photochemical reaction of the chromophoric systems upon sensitized and direct irradiation has also been presented. A highly unusual behavior of the chromophoric systems upon sensitized irradiation has also been presented.

1. Introduction

Polyquinanes in general have stimulated a long and sustained interest over several decades by virtue of their molecular architecture and biological properties.[1–3] Of various types, a large number of natural products contain linearly fused triquinane ring system such as **1** (Fig. 1). Angularly fused triquinane ring system of type **2** is also present in naturally occurring sesquiterpenes such as isocomenes, pentalenenes, silphinane in addition to others.[1,2] Basar and co-workers have isolated a novel sesquiterpene ventricosene **3** (Fig. 1) having angularly fused triquinane ring system in its structure from the essential oils of the liverwort *Lophozia ventricosa*.[4a] More sesquiterpenes containing angular triquinanes were isolated by Arnold and co-workers.[4b] Recently, a synthesis of ventricosene employing a gold catalyzed ring expansion has been reported.[5]

While a number of methods are known for the synthesis of linearly fused tricyclopentanoids, only a few routes have been developed for angularly fused triquinanes. We have a longstanding interest in the synthesis of bridged polycyclic compounds containing β,γ-enone chromophore and their photochemical transformation leading to various types of ring fused molecular structures in highly stereoselective manner.[6]

In order to extend our earlier approach to angular polyquinanes[7] and the current interest in synthesis of ventricosene, we considered developing synthesis of triquinane of type **4** having quaternary centre bearing geminal dimethyl group in one of the five membered rings via photochemical 1,2-acyl shift in embellished tricyclic compound **6**. Moreover, it was also interesting to explore 1,3-acyl shift in enone **6** that would provide tricyclic compounds of type **5** since functionalized hydrindanes fused with a cyclobutane ring are potential precursors for synthesis of various types of carbocycles including polyquinanes.[8]

We wish to report herein synthesis of tricyclic compounds of type **6** from *o*-hydroxymethyl phenol **7** via oxidative dearomatization, cycloaddition and studies on the photochemical reactions of **6** upon sensitized (3T) and singlet (1S) excitation.

2. Results and discussion

In order to realize the above objective, *o*-hydroxymethyl phenol **7** was required. It was considered that the alkylation of 5-methoxyindanone **8** to ketone **9** followed by reduction of the carbonyl group would give methoxyindane **10** that upon demethylation and hydroxymethylation would provide the compound **7**.

* Corresponding author.
E-mail address: vks@chem.iitb.ac.in (V. Singh).

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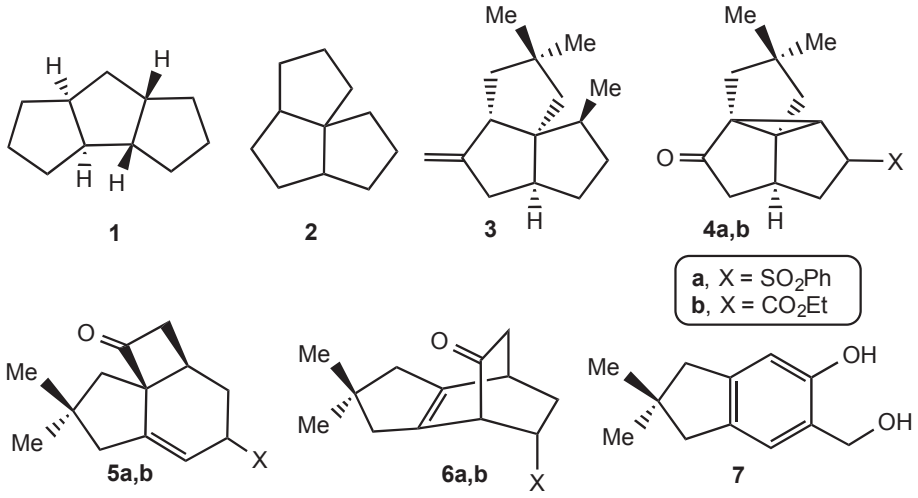


Fig. 1. Polyquinanes and precursors.

The dimethylated indanone **9** has been prepared earlier by alkylation of **8** with methyl iodide in the presence of KO^{t}Bu.[9] We prepared compound **9** by methylation of **8** in the presence of NaH-THF in excellent yield (Scheme 1). The reduction of the carbonyl group in **9** turned out to be not as simple as it appeared. Reaction of **9** under Wolf-Kishner condition[10] and reduction with Et_3SiH in the presence of CF_3SO_3H and/or TMS-OTf was not fruitful, and gave only unreacted starting material.[11] Attempted reduction of ketone **9** with H_2, Pd/C[12] was also unsuccessful.

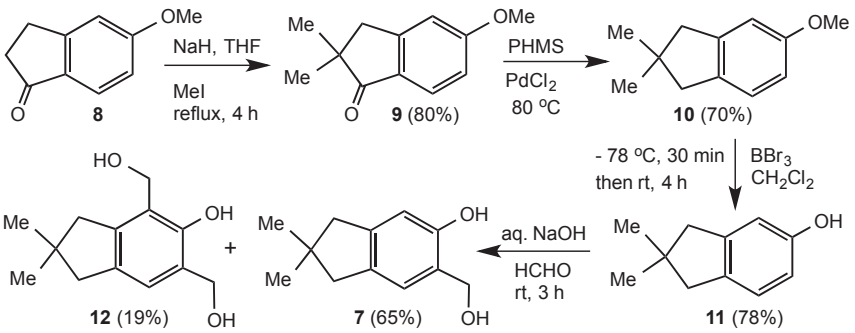
Finally, treatment of ketone **9** with polymethylhydrosiloxane (PHMS)[13] in the presence of $PdCl_2$ gave the compound **10** in good yield. Demethylation of **10** with BBr_3 furnished the phenol **11** that upon hydroxymethylation gave the required *o*-hydroxymethyl phenol **7** along with a minor amount of the product **12** (Scheme 1).

After having prepared the *o*-hydroxymethyl phenol **7**, its oxidative dearomatization to spiroepoxycyclohexa-2,4-dienone **13** and interception with phenylvinyl sulphone was attempted. Hence, a solution of compound **7** and phenyl vinyl sulphone was treated with sodium metaperiodate[14] according to our procedure developed earlier.[15] However the adduct **16a** was not obtained, the cyclohexadienone **13** was isolated instead. Therefore, the bicyclic spiroepoxycyclohexa-2,4-dienone **13** was heated with phenyl vinyl sulphone in a sealed tube which furnished the tricyclic keto-epoxide **16a** as a major product along with the aldehyde **15** (Scheme 2). The aldehyde **15** arises due to the rearrangement of oxirane ring in **13** followed by aromatization. Similarly, heating the cyclohexadienone **13** with ethyl acrylate also gave the adduct **16b** in good yield.

It was rather surprising to isolate the annulated spiroepoxycyclohexa-2,4-dienone **13** during the above oxidation especially since cyclohexa-2,4-dienones have transient existence and undergo instantaneous Diels-Alder dimerization.[6c,e,14] Indeed, a similar spiroepoxycyclohexa-2,4-dienone which is devoid of geminal methyl groups in the five membered ring, is known to undergo rapid Diels-Alder dimerization.[7a]

The cyclohexadienone **13** was reluctant to dimerize, it was fairly stable and could be thoroughly characterized. The reluctance of cyclohexa-2,4-dienone **13** towards dimerization is presumably a manifestation of the steric effect of geminal methyl group present in the five membered ring and proved beneficial as it provided a direct access to desired keto-epoxides **16a**,**b**.

The structure of the adduct **16a** was established from the following spectroscopic features. The IR spectrum of the adduct **16a** showed absorption band at 1739 cm^{-1} due to the presence of carbonyl group. The ^{1}H NMR (400 MHz) spectrum of **16a** displayed signals at δ 7.87 (d, J = 7.5 Hz, 2H), 7.66 (overlapped dd, $J_1 = J_2 = 7.5$ Hz, 1H) and 7.58 (overlapped dd, $J_1 = J_2 = 7.5$ Hz, 2H) for five aromatic proton of the sulphone moiety which indicated that cycloaddition had occurred. It further showed highly characteristic signals at δ 3.17 (part of an AB system, $J_{AB} = 5.9$ Hz, 1H) and at δ 2.88 (part of an AB system, $J_{AB} = 5.9$ Hz, 1H) due to protons of the oxirane ring. The signals due to methyl groups were observed at δ 1.23 (s, 3H) and 1.10 (s, 3H). In addition, signals were displayed at δ 3.69–3.63 (m, 2H), 2.67–2.63 (m, 1H), 2.60–2.53 (d, J = 15.5 Hz, 1H), 2.48–2.22 (m, 4H), 2.15 (dd, $J_1 = 13.2$ Hz, $J_2 = 6.1$ Hz, 1H) due to other methine and methylene protons. The ^{13}C NMR (100 MHz)



Scheme 1. Preparation of the aromatic precursor **7**.