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Note

Easy synthesis of heterocyclic carbene complexes by activation of chalcogenopyrones and benzopyrones to pyrylium salts and subsequent addition of carbanion of methoxy(methyl)pentacarbonyltungsten carbene complex ☆

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Abstract

Methylenechalcogenopyran and benzopyran Fischer carbene complexes are easily obtained from commercially available chalcogenopyrones or benzopyrones and carbanion of methoxy(methyl)carbene tungsten complex. The key of the heterocyclic carbene formation is the activation of the carbonyl group by alkylation with alkyl trifluoromethanesulfonate reagent.

Keywords: Methylenechalcogenopyran and benzopyran carbene complexes; Pyrylium salts; Chalcogenopyrone and benzopyrone

1. Introduction

As their tetrachalcogenofulvene isoelectronic analogues [1], the bichalcogenopyrans form, with various acceptors charge transfer complexes [2] possessing interesting electrical and magnetic properties. However, in comparison with the large studies about the TTF (Tetrathiafulvalene) and related heterocyclic compound chemistry during the past twenty years [1], few works were devoted to electron rich bipyran molecules [3]. Some of us have recently reported on the synthesis of electron rich extended bichalcogenopyrans and benzopyrans bearing methoxy groups in the ethylenic spacer. These compounds were obtained from a Pd° catalytic coupling reaction of α and γ-methylenechalcogenopyran and methylenebenzochalcogenopyran Fischer carbene complexes (Scheme 1) [4]. Most of these complexes, which are the key of the electron rich molecule formation, are synthetized from a condensation reaction between carbanions of Fischer-type carbene complexes [5] and γ-unsubstituted pyrylium salts (Scheme 1) [6].

The second step of this reaction, which implies a hydride departure, requires the use of triphenyl carbenium salt as an oxidant. As the pentacarbonylmetal fragment is sensitive to oxidant reagents, the heterocyclic carbene complexes are isolated in moderate to low yield [6].

Therefore, to tentatively improve the yield, and to obtain carbene complexes with new methylenechalcogenopyran and benzopyran heterocyclic nuclei, we wished to develop an expedient route to these compounds, using commercially available α and γ-chalcogenopyrones and benzopyrones. It is well established that methylation or silylation of the nucleophilic carbonyl oxygen atom of these substrates increases the reactivity towards nucleophile

☆ To the memory of Dr. Pierre GUENOT, Director of the Centre Régional de Mesures Physiques de l'Ouest – Université de Rennes 1.

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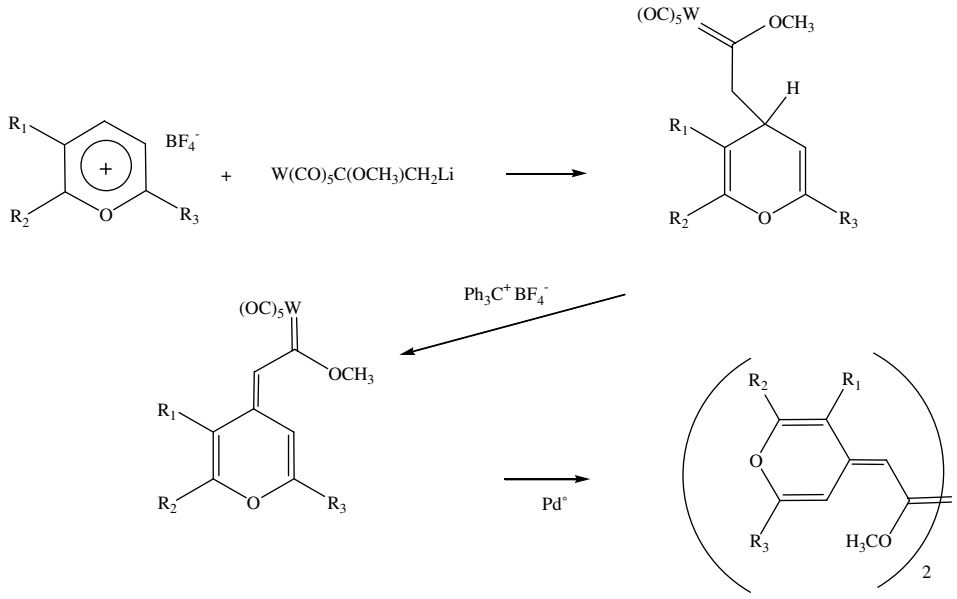


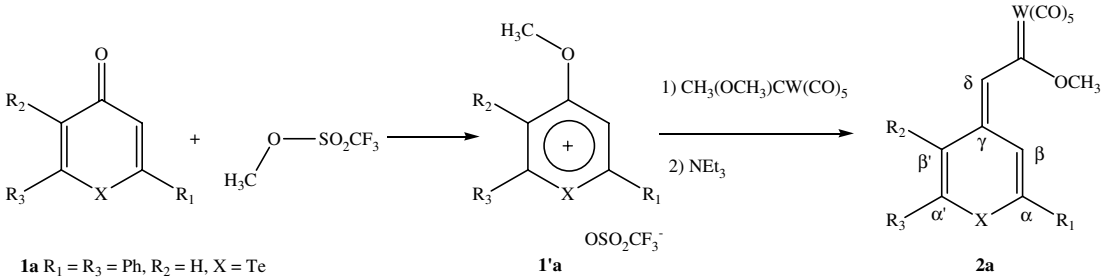
Scheme 1. Access to extended bipyrans from pyrylium salts and carbene complex.

addition, due to the formation of highly electrophilic α or γ-alkoxychalcogenopyrylium and benzopyrylium salts [7]. In this particular case the presence of the leaving alkoxy group should allow the formation of the methylenechalcogenopyran and benzopyran carbene complexes without the oxidation step. Recently, following a similar experimental procedure, we successfully obtained good yield of dithiafulvene carbene complexes from dithiolium salts bearing a leaving thiomethyl group [8].

2. Results and discussion

To test this synthetic methodology in the chalcogenopyrone and chalcogenobenzopyrone series, we first chose to consider the case of 2,6-diphenyltelluropyrone (Scheme 2). Mixing the telluropyrone **1a**, with an excess of methyl trifluoromethanesulfonate in boiling CH_2Cl_2, afforded the 2,6-diphenyl-4-methoxytelluropyran trifluoromethanesulfonate salt **1′a** in 57% yield (white powder). Adding NEt_3 to a THF solution of **1′a** and methoxy(methyl)carbene tungsten complex instantly produced a color change from yellow to blue. After hydrolysis, extraction with ether, and chromatography (silicagel, eluent: ether/petroleum ether) the telluromethylenepyran carbene complex **2a** was isolated (81% yield). The same two-step process was then applied to commercially available 2,6-diphenylthiopyrone **1b**. Unfortunately, isolation of the corresponding 4-methoxythiopyrylium salt was unsuccessful because of the great sensitivity of this compound towards moisture. To overcome this difficulty, a one pot procedure was then attempted. Pyrone **1b** and excess of methyl trifluoromethane sulfonate were heated at 60 °C for 1 h. Excess of the alkylating reagent was removed under vacuum and the solid residue was dissolved in dry THF. The methoxy(methyl)carbene complex and NEt_3 were then added successively. The solution turned blue. After hydrolysis, extraction with ether, and chromatography (silicagel, eluent: ether/petroleum ether), the blue methylenethiopyran carbene complex **2b** was isolated (32% yield).

For comparison purposes, we performed a reaction in THF at −78 °C with the air sensitive 2,6-diphenylthiopyrylium tetrafluoroborate and the carbanion formed by BuLi



1a $R_1 = R_3 = Ph$, $R_2 = H$, X = Te
1b $R_1 = R_3 = Ph$, $R_2 = H$, X = S
1c $R_1 = Ph$, $R_2 = R_3 = (CH)_4$, X = S

1'a

2a
2b
2c

Scheme 2. Chalcogenomethylenepyran and benzomethylenepyran carbene complex formation.