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Efficient Reduction of Thiopyrylium Salts to Corresponding 2H- and 4H-Thiopyrans Under Solvent-Free Condition: Regioselectivity and Mechanism

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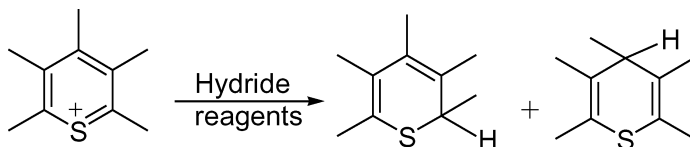
A solvent-free reduction of 2,4,6-triarylthiopyrylium with NaBH₄/alumina is described. The regioselectivity of these reductions were compared with those obtained in solution experiments.

Keywords Reduction; regioselectivity; sodium borhydride/alumina; solvent free; thiopyran; thiopyrylium

INTRODUCTION

Thiopyrylium cations have been the subject of a wide variety of practical applications. In particular a large number of technological studies involving thiopyrylium salts deal with their applications in the preparation of photosensitive compositions for electrophotographic, photoconductors, and optical recording media. These salts also show biological activity and find applications in medicine.¹

The reduction of these salts to their corresponding 2H- and 4H-thiopyrans can be accomplished with complex hydrides. Hydride donors can attack thiopyrylium salts either in the α -position, giving rise to a corresponding 2H-thiopyran, or in γ -position, leading to 4H-thiopyran.



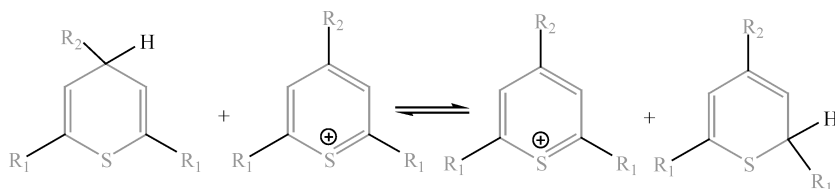
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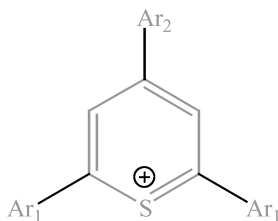
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A number of reductions have been carried out with NaBH_4 . Reduction of 2,4,6-triphenylthiopyrylium ions with NaBH_4 affords a 3:7 mixture of 2H and 4H isomers in methanol² and a 1:1 mixture in acetonitrile.³ 2,6-Diphenylthiopyrylium cations have been reduced in methanol in the ratio 0:100 for (2H:4H). Pentaphenylthiopyrylium ions undergo reduction with LiBH_4 in THF to yield the corresponding 4H-thiopyran in 30% yield.⁴

Thiopyrylium ions can function as catalysts in the equilibrium isomerization between the corresponding 2H- and 4H- as shown in the following equation.



In the course of our studies on synthesis and photoisomerization of 4H-thiopyrans,^{5,6} and our new interest in using solvent-free conditions as an efficient media,⁷ we decided to examine the reduction of some of triarylthiopyrylium salts under this condition (NaBH_4 /alumina) and then compare the results with those obtained in solution experiments.



$\text{Ar1}=\text{Ar2}=\text{Ph}$

$\text{Ar1}=\text{ph}, \text{Ar2}=(\text{p-Me})\text{C}_6\text{H}_4$

$\text{Ar1}=\text{Ph}, \text{Ar2}=(\text{p-OMe})\text{C}_6\text{H}_4; \text{Ar1}=(\text{p-OMe})\text{C}_6\text{H}_4, \text{Ar2}=\text{Ph}$

$\text{Ar1}=\text{Ph}, \text{Ar2}=(\text{p-NMe}_2)\text{C}_6\text{H}_4; \text{Ar1}=(\text{p-NMe}_2)\text{C}_6\text{H}_4, \text{Ar2}=\text{Ph}$

EXPERIMENTAL

All reagents were used from Merck Co. or Aldrich Co. TLC was performed on silica gel plate. ^1H NMR spectra were recorded in CDCl_3 on a Bruker 400 MHz spectrometer using TMS as an internal standard. A domestic microwave used for synthesis of pyrylium precursors. IR spectra were recorded on IR Shimadzu spectro was photometer.

Syntheses

All triarylthiopyrylium perchlorates were synthesized from the corresponding pyrylium salts, which were prepared in our new method with microwave irradiation,⁷ using the Ulrich and Wizinger method.⁸

General Procedure of Reduction

a) Solvent-Free Condition

1.25 mmol of NaBH₄ was added to 1 gr of alumina, after homogenizing 1 mmol of each thiopyrylium salt gradually added in portion, the mixtures were grinded in mortar, the reaction followed by tlc using hexane:ether (90:10 v/v) until conversion was complete, and then was worked up with n-hexane.

b) In Methanol

1.25 mmol of NaBH₄ was gradually added to a suspension of 1 mmol of each thiopyrylium salt in 5 ml methanol, maintained at -10 to -15°C after evaluating the hydrogen, the solution was worked up by evaporating the solvent.

RESULTS AND DISCUSSION

We investigated the reducing ability of NaBH₄/alumina for reduction of triarylthiopyrylium perchlorate. According to our knowledge this is the first report for the reduction of thiopyrylium in the solid state. The important role of alumina is apparent from the fact that only poor yields were obtained without this support. A simple extraction of the product from the solid support affords the corresponding 2H-thiopyrans as major products. In some cases the reduction of thiopyrylium salts is complete after few minutes (~10 min) of grinding. However, the reduction of the substrates bearing electron-donating substituents in the 2 and 6 positions is relatively slow in comparison with those with electron-donating groups in 4 position and 2,4,6-triphenylthiopyrylium as model compound. ¹H-NMR study of the product mixture revealed that reduction under solvent-free conditions also exhibit higher regioselectivity than those run in methanol, exemplified by the case of 2,4,6-triphenylthiopyrylium perchlorate under solvent-free conditions in which thermodynamically more stable corresponding 2H-thiopyran was obtained >95% while in methanol a 3:7 mixture of 2H and 4H isomers was obtained.

In conclusion, we have developed a facile and practical method for the reduction of triarylthiopyrylium salts with high regioselectivity and

this reveals that the hydride transfer might have occurred in this condition as well as in solvent.

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