

## Research Article

# High-Speed Reduction of Triarylpyrylium Salts Using $\text{Zn}(\text{BH}_4)_2/\text{SiO}_2$ as an Efficient and Regiospecific Reducing Reagent

Arash Mouradzadegun, Ali Reza Kiasat, and Somayeh Elahi

Department of Chemistry, Faculty of Science, University of Shahid Chamran, Ahvaz 6135743151, Iran

Correspondence should be addressed to Arash Mouradzadegun; arash\_m@scu.ac.ir

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The regiospecific reduction of some triarylpyrylium salts in the presence of modified hydride donors was investigated. Among these reagents,  $\text{Zn}(\text{BH}_4)_2/\text{SiO}_2$  performed the best results. The major advantages of this reagent are the cheapness, availability, simplicity in operation, very short reaction time and much improved regioselectivity in comparison with the other reducing reagents.

## 1. Introduction

The selective reduction is a real challenge in organic synthesis. The selectivity is generally achieved by the use of modified reducing reagents which are formed by the replacement of hydride with sterically bulky substituents or electron-withdrawing groups [1–4]. Thus to achieve this goal, currently the use of modified hydride donors has been expanded [5–8].

The reduction of trialkyl and triphenylpyrylium salts in the presence of hydride donors especially  $\text{NaBH}_4$  has been extensively studied [9–12]. In addition to reduction by hydride transfer, a one-electron reduction by zinc is possible leading exclusively to 4,4'-bis-pyran dimmers [13]. Hydride donors can attack to pyrylium salts either in the  $\alpha$ -position, giving rise to a corresponding dienone (I), or in  $\gamma$ -position, leading to 4H-pyran (II) (Scheme 1). To the best of our knowledge no other example of selective reduction of triarylpyrylium salts has been published to date.

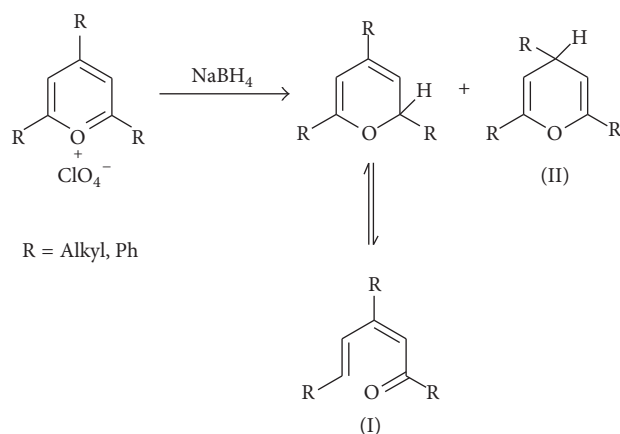
So in connection with this trend and in continuation with our studies to develop selective, preparative, and synthetically useful methodology for preparation [14], application [15, 16], and other transformations of various pyrylium and thiopyrylium salts [17–20], here we wish to report regiospecific

reduction of triarylpyrylium salts carrying electron-donor or withdrawing groups on phenyl substitutions of 2,4,6-positions of pyrylium ring with some of the modified hydride donors such as  $\text{Zn}(\text{BH}_4)_2$ ,  $\text{Zn}(\text{BH}_4)_2/\text{SiO}_2$ , borohydride supported on ion exchange resin (BER), and sulfureted borohydride ion exchange resin (SBER). We do hope that these new reagents could perform more efficiency beside facile methodology for regiospecific reduction of triarylpyrylium salts.

## 2. Experimental

Chemicals were purchased from Fluka, Merck, and Aldrich chemical companies. Monitoring of the reactions was accomplished by TLC. IR spectra were obtained on a Bomen MB: 102 FT IR spectrophotometer.  $^1\text{H}$ NMR spectra were recorded on 400 MHz Bruker using  $\text{CDCl}_3$  as the solvent and TMS as the internal standard.

**2.1. Syntheses.** All triarylpyrylium perchlorates were synthesized from the corresponding aldehydes and ketones by the method previously described [21, 22].



SCHEME 1: Reduction of trialkyl and triphenylpyrylium salts in the presence of  $\text{NaBH}_4$ .

## 2.2. Preparation of Reducing Reagents

**2.2.1. Borohydride Supported on Ion Exchange Resin.** Amberlite IRA-400 (chloride form) (1 g) was washed several times with distilled water to remove foreign materials. The resin was stirred in a 20% aqueous sodium borohydride solution (100 mL) for 20 min. It was then filtered and washed several times with water. The resin was finally dried over anhydrous  $\text{P}_2\text{O}_5$  for 5 h under vacuum at  $50^\circ\text{C}$ .

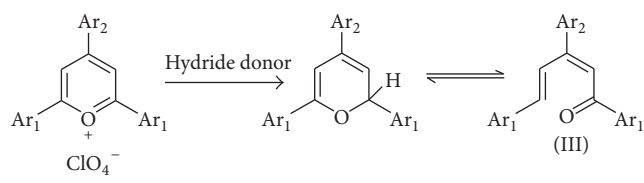
**2.2.2. Sulfurated Borohydride Ion Exchange Resin.** Sulfur power (1 mmol) and borohydride exchange resin (prepared by the previous procedure) was added in methanol (5 mL) and stirred until colour of resin becomes red (15–20 min), ensuring that BER changed to sulfurated borohydride ion exchange resin (SBER).

**2.2.3. Zinc Borohydride.** To sodium borohydride (0.8 g) in redistilled diethylether (25 mL) was added recently fused zinc chloride (1.7 g). The mixture was stirred at  $0\text{--}5^\circ\text{C}$ . After filtration, the clear solution was used immediately.

**2.2.4. Zinc Borohydride Supported on Silica Gel.** A solution of zinc borohydride (3 mmol) in diethylether was added to silica gel (1 g) and stirred at room temperature for 30 min. Solvent was then evaporated off under vacuum to give the supported reagent which was used for reduction of substrate on the same day.

## 2.3. General Procedure

- (1) The reaction of 1 mmol triphenylpyrylium perchlorate in the presence of 1 mmol of various reducing reagents was investigated in THF and  $\text{CH}_3\text{OH}$  (2 mL). The reaction followed by TLC until conversion was completed, then reaction mixture was filtered, and the product was worked up by evaporating the solvent.



$\text{Ar}_1$ :  $\text{C}_6\text{H}_5$ ,  $\text{C}_6\text{H}_4(p\text{-OMe})$

$\text{Ar}_2$ :  $\text{C}_6\text{H}_5$ ,  $\text{C}_6\text{H}_4(p\text{-Me})$ ,  $\text{C}_6\text{H}_4(p\text{-OMe})$ ,

$\text{C}_6\text{H}_4(p\text{-NMe}_2)$ ,  $\text{C}_6\text{H}_4(p\text{-Cl})$ ,  $\text{C}_6\text{H}_4(p\text{-NO}_2)$

Hydride donor:  $\text{NaBH}_4$ ,  $\text{Zn}(\text{BH}_4)_2$ ,  $\text{Zn}(\text{BH}_4)_2/\text{SiO}_2$ ,  
borohydride supported on ion exchange resin (BER),  
sulfurated borohydride ion exchange resin (SBER)

SCHEME 2: Regiospecific reduction of triarylpyrylium salts in the presence of various hydride donors.

- (2) The reaction of other triarylpyrylium perchlorates (1 mmol) was done with zinc borohydride supported on silica gel (1 mmol), as the best reagent, in THF (2 mL). The reaction followed by TLC until conversion was completed, then reaction mixture was filtered, and the product was worked up by evaporating the solvent. The structure of these compounds was confirmed by IR,  $^1\text{H}$ NMR, and physical data (m.p.).

## 3. Results and Discussion

In efforts to regiospecific reduction of triarylpyrylium salts to corresponding dienones (III) as only product, these transformations were studied by various hydride donors (Scheme 2).

Initially to achieve optimal conditions, the transformation of 1 mmol triphenylpyrylium perchlorate (as the model compound) was investigated with various hydride donors (1 mmol) in different solvent such as THF and  $\text{CH}_3\text{OH}$  according to the hydride donor (Table 1).

As shown in Table 1, selectivity has not been observed in cases of 1 to 3, and both products, dienone and 4H-pyran, were obtained. This may be described by considering the fact that selectivity of hydride ion depends on the counter ion.

The results reveal that  $\text{Zn}(\text{BH}_4)_2$  and  $\text{Zn}(\text{BH}_4)_2/\text{SiO}_2$  are both potentially more selective reagents, because these new hydride donors, attack to triphenylpyrylium salt only in  $\alpha$ -position, leading to corresponding 2H-pyran which is converted to dienone as only product. Between these two reagents,  $\text{Zn}(\text{BH}_4)_2$  showed less stability, so, in spite of shorter reaction time,  $\text{Zn}(\text{BH}_4)_2/\text{SiO}_2$  was selected as the best choice.

The generality of this process was illustrated with various triarylpyrylium perchlorate carrying electron-donor or withdrawing groups on phenyl substitutions of 2,4,6-positions of pyrylium ring in the presence of  $\text{Zn}(\text{BH}_4)_2/\text{SiO}_2$  in which corresponding dienones with good yields and very short reaction times were synthesized (Table 2).

It is necessary to note that such modified hydride donor that exhibited longer reaction time for model compound

TABLE 1: Comparing the ability of different hydride donors for reduction of triphenylpyrylium salts in various solvent.

Entry	Reducing reagent	Solvent	Time	Results
1	NaBH <sub>4</sub>	THF	1 h	Dienone and 4H-pyran
2	BER	THF	4 h	Dienone and 4H-pyran
3	SBER	CH <sub>3</sub> OH	4 h	Dienone and 4H-pyran
4	Zn (BH <sub>4</sub> ) <sub>2</sub>	THF	Imm.	Dienone
5	Zn (BH <sub>4</sub> ) <sub>2</sub> /SiO <sub>2</sub>	THF	5 min	Dienone

Imm: immediately (1 min).

TABLE 2: Reaction of pyrylium salts with Zn(BH<sub>4</sub>)<sub>2</sub>/SiO<sub>2</sub>.

Entry	Substrate	Product	Yield (%)	Time ( min)
1			98	5
2			85	3
3			92	3
4			97	Imm.
5			79	Imm.
6			92	Imm.
7			89	Imm.
8			90	Imm.
9			82	Imm.

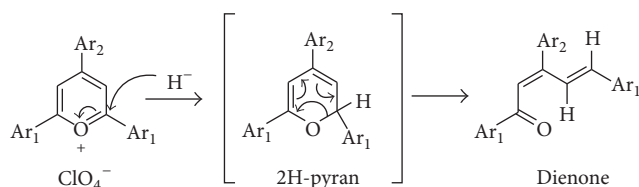
Imm: immediately (1 min).

allows to reach unusual shorter reaction time for other triarylpyrylium salts ( entries 4–9).

The stereochemistry of the ring opening product was found to be in the trans configuration as determined from the coupling constants associated with the <sup>1</sup>H NMR spectral resonances of the ring protons in. Because of actually not characterized form of modified reagent the only H<sup>-</sup> was used for selective attacking (Scheme 3).

## 4. Conclusions

Zinc borohydride supported on silica gel provide an inexpensive and efficient methodology for the regiospecific reduction of triarylpyrylium salts. Moreover, the mildness, convenience, stability, and high yield will make these simple reagents more useful and attractive in this methodology.



SCHEME 3: Stereochemistry of product.

## 5. Physical and Spectral Data

(1) *1,3,5-Triphenyl-penta-2,4-dien-1-one*. Yellow crystals, m.p.: 120°C (from EtOH); yield 98%; IR (neat):  $\nu_{\text{CO}}$  (1646 cm<sup>-1</sup>). <sup>1</sup>HNMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 6.74 (H<sub>1</sub>, d,  $J$  = 16 Hz), 6.89 (H<sub>3</sub>, s), (7.31–7.57), 8.03 (15H, m, Ar-H), 8.53 (H<sub>2</sub>, d,  $J$  = 16 Hz).

(2) *1,5-Diphenyl-3-p-tolyl-penta-2,4-dien-1-one*. Oil, yield 85%; IR (neat):  $\nu_{\text{CO}}$  (1638 cm<sup>-1</sup>). <sup>1</sup>HNMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 2.48 (3H, s, CH<sub>3</sub>), 6.71 (H<sub>1</sub>, d,  $J$  = 16 Hz), 6.82 (H<sub>3</sub>, s), (6.89–7.49), 8.02 (14H, m, Ar-H), 8.44 (H<sub>2</sub>, d,  $J$  = 16 Hz).

(3) *1,5-Bis-(4-methoxy-phenyl)-3-phenyl-penta-2,4-dien-1-one*. Oil, yield 92%; IR (neat):  $\nu_{\text{CO}}$  (1638 cm<sup>-1</sup>). <sup>1</sup>HNMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 3.88 (6H, s, OCH<sub>3</sub>), 6.82 (H<sub>1</sub>, d,  $J$  = 16 Hz), 6.91 (H<sub>3</sub>, s), 7.02, (7.34–7.57), 8.01 (13H, m, Ar-H), 8.26 (H<sub>2</sub>, d,  $J$  = 16 Hz).

(4) *3-(4-Methoxy-phenyl)-1,5-diphenyl-penta-2,4-dien-1-one*. Yellow crystals, m.p.: 110°C (from EtOH); yield 92%; IR (neat):  $\nu_{\text{CO}}$  (1648 cm<sup>-1</sup>). <sup>1</sup>HNMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 3.86 (3H, s, OCH<sub>3</sub>), 6.82 (H<sub>1</sub>, d,  $J$  = 16.2 Hz), 6.90 (H<sub>3</sub>, s), 7.02, (7.34–7.57), 8.01 (14H, m, Ar-H), 8.47 (H<sub>2</sub>, d,  $J$  = 16.2 Hz).

(5) *1,5-Bis-(4-methoxy-phenyl)-3-p-tolyl-penta-2,4-dien-1-one*. Oil, yield 79%; IR (neat):  $\nu_{\text{CO}}$  (1635 cm<sup>-1</sup>). <sup>1</sup>HNMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 2.46 (3H, s, CH<sub>3</sub>), 3.87 (6H, s, OCH<sub>3</sub>), 6.71 (H<sub>1</sub>, d,  $J$  = 16.4 Hz), 6.82 (H<sub>3</sub>, s), (6.86–7.49), 8.02 (12H, m, Ar-H), 8.44 (H<sub>2</sub>, d,  $J$  = 16.4 Hz).

(6) *1,3,5-Tris-(4-methoxy-phenyl)-penta-2,4-dien-1-one*. Oil, yield 92%; IR (neat):  $\nu_{\text{CO}}$  (1638 cm<sup>-1</sup>). <sup>1</sup>HNMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 3.88 (9H, s, OCH<sub>3</sub>), 6.82 (H<sub>1</sub>, d,  $J$  = 16.2 Hz), 6.91 (H<sub>3</sub>, s), 7.02, (7.28–7.57), 8.02 (12H, m, Ar-H), 8.26 (H<sub>2</sub>, d,  $J$  = 16.2 Hz).

(7) *3-(4-Dimethylamino-phenyl)-1,5-diphenyl-penta-2,4-dien-1-one*. Red crystals, m.p.: 130°C (from EtOH); yield 89%; IR (neat):  $\nu_{\text{CO}}$  (1637 cm<sup>-1</sup>). <sup>1</sup>HNMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 2.46 (6H, s, N(CH<sub>3</sub>)<sub>2</sub>), 6.71 (H<sub>1</sub>, d,  $J$  = 16.2 Hz), 6.89 (H<sub>3</sub>, s), 7.37–7.49, 8.02 (14H, m, Ar-H), 8.44 (H<sub>2</sub>, d,  $J$  = 16.2 Hz).

(8) *3-(4-Chloro-phenyl)-1,5-diphenyl-penta-2,4-dien-1-one*. Yellow crystals, m.p.: 112°C (from EtOH); yield 90%; IR (neat):  $\nu_{\text{CO}}$  (1649 cm<sup>-1</sup>). <sup>1</sup>HNMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 6.71 (H<sub>1</sub>, d,  $J$  = 16.4 Hz), 6.72 (H<sub>3</sub>, s), 7.33–7.58, 8.01 (14H, m, Ar-H), 8.48 (H<sub>2</sub>, d,  $J$  = 16.4 Hz).

(9) *3-(4-Nitro-phenyl)-1,5-diphenyl-penta-2,4-dien-1-one*. Brown crystals, m.p.: 115°C (from EtOH); yield 82%; IR

(neat):  $\nu_{\text{CO}}$  (1649 cm<sup>-1</sup>), NO<sub>2</sub> (1345, 1518 cm<sup>-1</sup>). <sup>1</sup>HNMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 6.71 (H<sub>1</sub>, d,  $J$  = 16.2 Hz), 6.89 (H<sub>3</sub>, s), 7.28–7.58, 8.01 (14H, m, Ar-H), 8.48 (H<sub>2</sub>, d,  $J$  = 16.2 Hz).

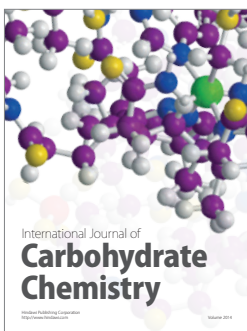
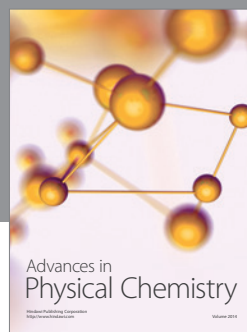
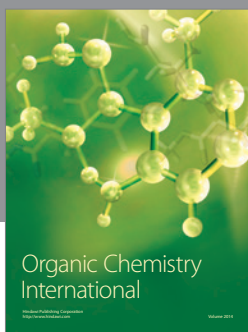
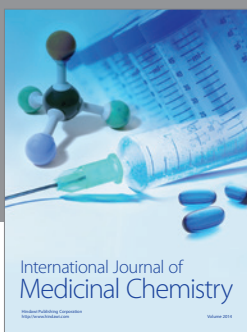
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