



Preparation of 1,1-diacetates from aldehydes by LiBH_4 and Ac_2O in the presence of cation exchange resin

REZA REZAEKHORDEHFOROSH, BEHROOZKHEZRI and DAVOOD SETAMDIDEH*

Department of Chemistry, Mahabad Branch, Islamic Azad University, Mahabad, Iran.

*Corresponding author E-mail: davood.setamdideh@gmail.com; d.setamdideh@iau-mahabad.ac.ir

<http://dx.doi.org/10.13005/ojc/310278>

(Received: November 05, 2015; Accepted: January 01, 2015)

ABSTRACT

A variety of 1,1-diacetates have been produced from the corresponding aldehydes (1 mmol) by LiBH_4 (1.25 mmol) and Ac_2O (1 mL) in the presence of DOWEX(R)50WX4 (0.5 g) as a cation exchange resin within 10 min at room temperature with excellent yields of the products (93-97%).

Key words: LiBH_4 , cation exchange resin, acylal, *gem*-diacetate, Ac_2O

INTRODUCTION

Carbonyl functional group of aldehydes has been protected in organic synthesis by the preparation of 1,1-diacetates (*gem*-diacetates, acylals) from the corresponding aldehydes¹⁻² because 1,1-diacetates are stable under neutral, basic and critically controlled acidic conditions. Also, these compounds have been used as starting materials for Diels-Alder reactions³, Grignard^{4a}, Barbier^{4b}, Prins reactions⁵, Knoevenagel^{6a} and benzoin condensation.^{6b} 1,1-diacetates are also used in the synthesis of chrysanthemoid acid^{7a}, sphingofungins E & F^{7b} and were utilized as cross linking reagents in cotton². Several methods⁸⁻⁵⁰ have been employed for the synthesis of 1,1-diacetates. These methods have some disadvantages such as use of strong acids, moisture sensitivity, high toxicity, high cost of the

reagents, unavailable catalyst, harsh reaction conditions and long reaction times. So, the research for new methods for the preparation of 1,1-diacetates is still of importance. This subject encourages us to investigate the preparation of 1,1-diacetates from the corresponding aldehydes in continuation of our research programs⁵¹⁻⁵⁹. Herein, We now report the results of a parallel investigation for the fast and efficient method for the synthesis a variety of 1,1-diacetates with $\text{LiBH}_4/\text{Ac}_2\text{O}$ in the presence of DOWEX(R)50WX4 as a cation exchange resin. Former, NaBH_4 ⁵⁸ and $\text{Zn}(\text{BH}_4)_2$ ⁵⁹ have been proposed as a co-reactant.

RESULTS AND DISCUSSION

DOWEX (cation exchange resin) as catalyst has been used for the synthesis of Oximes,

⁵¹ reduction of carbonyl compounds, ⁵² synthesis of cyanohydrins ⁵³ and reductive-amination of aldehydes⁵⁴. In this context, we have used it for efficient and facile preparation of 1,1-diacetates by $\text{LiBH}_4/\text{Ac}_2\text{O}/\text{DOWEX(R)50WX4}$ at room temperature.

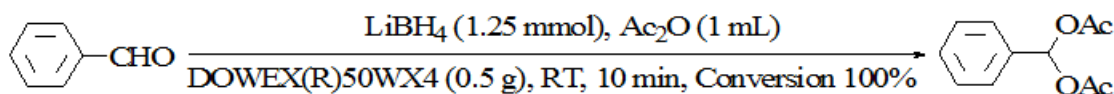
Benzaldehyde as a model compound has been selected. The reaction of benzaldehyde was carried out in different amounts of LiBH_4 , Ac_2O , DOWEX(R)50WX4 and solvents for the selection of proper conditions at room temperature. Different solvents (THF, diethyl ether, CH_2Cl_2 , CH_3CN , *n*-hexane, Ac_2O , THF- Ac_2O , $\text{Ac}_2\text{O}-\text{CH}_3\text{CN}$,...) have been tested. We have observed the reaction was most facile and proceeded to give the highest yield in Ac_2O . The optimization reaction conditions showed that using 1.25 molar equivalents of LiBH_4 and 0.5 g of DOWEX(R)50WX4 in 1 mL Ac_2O were the best conditions to complete the reaction of benzaldehyde (1 mmol) to 1,1-benzyl diacetate within 10 min with 93% yields of product as shown in scheme 1.

This protocol was further examined by using various structurally different aldehydes. The corresponding 1,1-diacetates were prepared in excellent yields (93-97%) within 10 min as shown in Table 1.

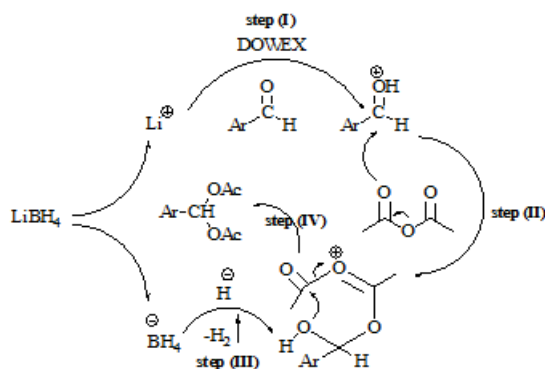
The proposed mechanism for the influence of LiBH_4 , Ac_2O and DOWEX has been shown in scheme II. It appears SO_3H groups on DOWEX (cation exchange resin, strong acid) protonate the carbonyl group of aldehydes (scheme II, step I). So the carbonyl group is more susceptible for Ac_2O attack (scheme II, step II). Also, LiBH_4 can promote the reaction by the hydride attack (scheme 2, step III).

Cinnamaldehyde as an enal has been converted to the corresponding cinnamyl diacetate in 95% yield as shown in scheme 3.

The $\text{C}=\text{O}$ stretching frequency in FT-IR spectrum appears around $1738\text{-}1763\text{ cm}^{-1}$. Also, the products were characterized by the ^1H -chemical



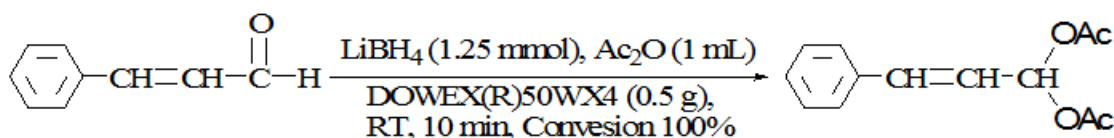
Scheme 1



Scheme 2

shift of the CH group which appears around 6.8-8 ppm as a singlet (1H) and 1,1-diacetates group which appears around 2.1 ppm as a singlet (6H).

Also, our experiments showed that ketones do not react with this system. The reusability of the catalyst has been checked by using the recovered DOWEX(R)50WX4 from the reactions. The experiments have shown that the recovered catalyst after regeneration (it was stirred in HCl 10-5% for 30-60 min, and then washed with distilled water) could be used like the first.



Scheme 3

Table 1: The preparation of 1,1-diacetates from aldehydes (1 mmol) by LiBH_4 (1.25mmol), Ac_2O (1 mL) & DOWEX(R)50WX4 (0.5 g) at RT

Entry	Aldehydes	Products	Time (min)	Yields (%) ^a	m.p. (°C) ^b
1	benzaldehyde	1,1-diacetoxy-1-phenyl methane	10	93	44-45
2	4-bromobenzaldehyde	1,1-diacetoxy-1-(4-bromophenyl) methane	10	97	94-95
3	2-chlorobenzaldehyde	1,1-diacetoxy-1-(2-chlorophenyl) methane	10	95	52-53
4	4-chlorobenzaldehyde	1,1-diacetoxy-1-(4-chlorophenyl) methane	10	95	83-84
5	3-chlorobenzaldehyde	1,1-diacetoxy-1-(3-chlorophenyl) methane	10	97	64-65
6	2,4-dichlorobenzaldehyde	1,1-diacetoxy-1-(2,4-dichlorophenyl) methane	10	97	99-101
7	4-nitrobenzaldehyde	1,1-diacetoxy-1-(4-nitrophenyl) methane	10	96	124-125
8	3-nitrobenzaldehyde	1,1-diacetoxy-1-(3-nitrophenyl) methane	10	95	66-67
9	4-methoxybenzaldehyde	1,1-diacetoxy-1-(4-methoxyphenyl) methane	10	95	65-66
10	3-methoxybenzaldehyde	1,1-diacetoxy-1-(3-methoxyphenyl) methane	10	96	oil
11	2-methoxybenzaldehyde	1,1-diacetoxy-1-(2-methoxyphenyl) methane	10	93	69-70
12	3,4-dimethoxybenzaldehyde	1,1-diacetoxy-1-(3,4-dimethoxyphenyl) methane	10	94	64-65
13	4-methylbenzaldehyde	1,1-diacetoxy-1-(4-methylphenyl) methane	10	94	80-81
14	cinnamaldehyde	1,1-diacetoxy-1-(cinammyl) methane	10	95	83-85

^aYields refer to isolated pure products. ^bThe melting points were compared with the literature.⁴⁶⁻⁵⁰

EXPERIMENTAL

General

The IR and ¹H NMR spectra were recorded on PerkinElmer FT-IR RXI, 300 MHz Bruker spectrometers, respectively. The products were characterized by their ¹H NMR, ¹³C NMR or IR spectra and comparison with authentic samples (melting points). All substrates and reagents were purchased from commercial sources with the best quality and used without further purification. All yields referred to isolated pure products.

Reaction of benzaldehyde with $\text{LiBH}_4/\text{Ac}_2\text{O}/\text{DOWEX(R)50WX4}$ system, A typical procedure

In a round-bottomed flask (5 mL) equipped with a magnetic stirrer, a mixture of benzaldehyde (0.106 g, 1 mmol), Ac_2O (1 mL) and DOWEX(R)50WX4 (0.5 g) was prepared. Then the LiBH_4 (0.028 g, 1.25mmol) was added to the reaction mixture and stirred at room temperature. TLC monitored the progress of the reaction (eluent; *n*-hexan/EtOAc: 9/1). The reaction was filtered after completion within 10 min. After completion of the reaction, the catalyst was filtered and washed with ethyl acetate (15 mL). The combined organic layers

were washed with saturated NaHCO_3 solution (3 × 10 mL) and water (10 mL) and then dried over anhydrous Na_2SO_4 . The solvent was removed on a rotary evaporator under reduced pressure to give pure product. 1, 1-diacetoxy-1-phenylmethane has been obtained (0.193 g, 93% yield, Table 1, entry 1) which was characterized by ¹H-NMR, ¹³C-NMR and FT-IR spectroscopy. ¹H-NMR (CDCl_3): δ 2.14 (s, 6H), 7.41-7.43 (Ar, 3H), 7.52-7.55 (Ar, 2H), 7.69 (s, 1H) ppm; ¹³C-NMR (CDCl_3): δ 20.85, 89.67, 126.65, 128.58, 129.74, 135.40, 169.79; IR (KBr) $\tilde{\nu}$ = 3021, 1761, 1373, 1243, 1216, 1009, 767 cm^{-1} .

CONCLUSION

In this context, we have shown that the $\text{LiBH}_4/\text{Ac}_2\text{O}/\text{DOWEX(R)50WX4}$ system is convenient for the preparation of 1,1-diacetates from aldehydes in high to excellent yields. The reactions were carried out with 1.25 molar equivalents of LiBH_4 and Ac_2O (1 mL) in the presence of 0.5 g DOWEX(R)50WX4 at room temperature. Shorter reaction times, easy work-up procedure makes as an attractive new protocol and it could be a useful addition to the present methodologies.

ACKNOWLEDGMENTS

The authors gratefully appreciated the financial support of this work by the research council of Islamic Azad University branch of Mahabad.

REFERENCES

- (a) Greene, T. W.; Wuts, P. G. M. *Protective Groups in Organic Synthesis*, 3rd Ed., Wiley-VCH, New York, **1999**; p 306..
- Frick, J. G.; Harper, R. J.; Jr. *J. Appl. Polymer Sci.***1984**, *29*, 1433-1447.
- Banks, R. E.; Miller, J. A.; Nunn, M. J.; Stanley, P.; Weakley, T. J. R.; Ullah, Z. *J. Chem Soc. Perkin Trans. 1*.**1981**, 1096-1102.
- (a) Sandberg, M.; Sydnes, L. K. *Tetrahedron Lett.***1998**, *39*, 6361-6364. (b) Sydnes, L. K.; Sandberg, M. *etrahedron***1997**, *53*, 12679-12690.
- (a) Mowry, D. T. *J. Am. Chem. Soc.***1950**, *72*, 2535-2537. (b) Merten, R.; Muller, G. *Angew. Chem.***1962**, *74*, 866-871.
- (a) Trost, B. M.; Vercauteran, J. *Tetrahedron Lett.* **1985**, *26*, 131-134. (b) Trost, B. M.; Lee, C. B.; Weiss, J. M. *J. Am. Chem. Soc.* **1995**, *117*, 7247-7248. (c) Sandberg, M.; Sydnes, L. K. *Org. Lett.***2000**, *2*, 687-689.
- (a) Kula, J. Pol. Pat. PL 143: 824,**1988**; (*Chem. Abstr.* 112, 216290y). (b) Trost, B. M.; Lee, C. J. *Am. Chem. Soc.***2001**, *123*, 12191-12201.
- Reddy, A. V.; Ravinder, K.; Reddy, V. L. N.; Ravikanth, V.; Yenkaeswarlu, Y. *Synth. Commun.***2003**, *33*, 1531-1536.
- Bandgar, B. P.; Makone, S. S.; Kulkarni, S. P. *Monatsh. Chem.***2000**, *131*, 417-420.
- Li, T. S.; Zhang, Z. H.; Gao, Y. J. *Synth. Commun.***1998**, *28*, 4665-4671.
- (a) Kumar, P.; Hegde, V. R.; Kumar, T. P. *Tetrahedron Lett.* **1995**, *36*, 601-602. (b) Pereira, C. B.; Gigante, M. J.; Marcelo-Curto, H.; Carreyre, G.; Perot, G.; Guisnet, M. *Synthesis***1995**, 1077-1078. (c) Ballini, R.; Bordoni, M.; Bosica, G.; Maggi, R.; Sartori, G. *Tetrahedron Lett.***1998**, *39*, 7587-7580.
- Olah, G. A.; Mehrotra, A. K.; *Synthesis***1982**, 962-963.
- Jin, T. S.; Du, G. Y.; Li, T. S. *Ind. J. Chem., Sec. B* **1998**, 939-940.
- Wang, C.; Li. M.; *Synth. Commun.***2002**, *32*, 3469-3473.
- Gowravaram, S.; Abraham S.; Ramalingam, T.; Yadav, J. S. *J. Chem. Res. (S)***2002**, *3*, 144-146.
- Deka, N.; Borah, R.; Kalita, D. J.; Sarma, J. C. *J. Chem. Res.(S)***1998**, 94-95.
- Agarwal, V. K.; Fonquerna, S. S.; Vennall, G. P. *Synlett***1998**, 849-850.
- Deka, N.; Kalita, D. J.; Borah, R.; Sarma, J. C. *J. Org. Chem.* **1997**, *62*, 1563-1564.
- Karimi, B.; Seradj, H.; Ebrahimian, R. G. *Synlett***2000**, 623-624.
- Michie, J. K.; Miller, J. A. *Synthesis***1981**, 824-824.
- Gregory, M. J. *J. Chem. Soc. B* **1970**, 1201-1207.
- Chandra, K. L.; Saravanan, P.; Singh, V. K. *Synlett***2000**, 359-360.
- Sumida, N.; Nishioka, K.; Sato, T. *Synlett***2001**, *12*, 1921-1922.
- Jin, T. S.; Sun, G.; Li, Y. W.; Li, T. S. *Green Chem.* **2002**, *4*, 255-256.
- Yadav, J. S.; Reddy, B. V. S.; Srinivas, Ch. *Synth. Commun.***2002**, *32*, 2169-2174.
- Roy, S. C.; Banerjee, B. *Synlett***2002**, 1677-1678.
- Karimi, B.; Maleki, J.; *J. Org. Chem.***2003**, *68*, 4951-4954.
- Ranu, B. C.; Dutta, J.; Das, A. *Chem. Lett.* **2003**, *32*, 366-367.
- Firouzabadi, H.; Iranpoor, N.; Nowrouzi, F.; Amani, K.; *Tetrahedron Lett.***2003**, *44*, 3951-3954.
- Smitha, G.; Reddy, Ch. S. *Tetrahedron***2003**, *59*, 9571-9576.
- Aggen, D. H.; Hayes, Arnold, J. N.; Hayes, P. D.; Smoter, N. J.; Mohan, R. S. *Tetrahedron***2004**, *60*, 3675-3679.
- Carrigan, M. C.; Eash, K. J.; Oswald, M. C.; Mohan, R. S. *Tetrahedron Lett.* **2001**, *42*, 8133-

- 8135.
33. Curini, M.; Epifano, F.; Marcotullio, M.C.; Rosati, O.; Nocchetti, M. *Tetrahedron Lett.* **2002**, *43*, 2709-2711.
34. Kumar, S.; Saini, A.; Sandhu, J. A. *Arkivok***2007**, *14*, 27-33.
35. Sun, P.; Hu, Z. *J. Chem. Res.* **2005**, *10*, 659-660.
36. Palacios-Grijalva, L. N.; Cruz-González, D.Y.; Lomas-Romero, L.; González-Zamora, E.; Ulibarri, G.; Negrón-Silva, G. E. *Molecules***2009**, *14*, 4065-4078.
37. Ghorbani-Vaghei, R.; Amiri, M.; Moshfeghifar, N.; Veisi, H.; Akbari Dadamahaleh, S. *J. Iran. Chem. Soc.* **2009**, *6*, 754-760.
38. Shirini, F.; Mamaghani, M.; Mostashari-Rad, T.; Abedini, M. *Bull. Korean Chem. Soc.***2010**, *31*, 2399-2401.
39. Mirjalili, B. F.; Zolfigol, M. A.; Bamoniri, A.; Sheikhan, N. *J. Chin. Chem. Soc.* **2006**, *53*, 955-959.
40. Zhang, X.; Li, L.; Zhang, G. *Green Chemistry***2003**, *5*, 646-468.
41. Dalpozzo, R.; Nino, A. D.; Maiuolo, L.; Nardi, M.; Procopio, A.; Russo, B.; Tagarelli, A. *Arkivoc***2006**, *6*, 181-189.
42. Shelke, k.; Sapkal, S.; Katagaonkar, A.; Shingate, B.; Shingare, M. S. *S. Afr. J. Chem.* **2009**, *62*, 109-112.
43. Negrón, E. E.; Palacios, L. N.; Angeles, D.; Lomas, L.; Gaviño, R. *J. Mex. Chem. Soc.***2005**, *49*, 252-256.
44. Heravi, M. M.; Bakhtiari, K.; Taheri, S.; Oskooie, H. A. *Green Chem.* **2005**, *7*, 867-869.
45. Pourmosavi, S. A.; Zinati, Z. *Turk. J. Chem.* **2009**, *33*, 385-392.
46. Yin, L.; Zhang, Z. H.; Wang, Y. M.; Pang, M. L. *Synlett***2004**, *10*, 1727-1730.
47. Khan, A. T.; Choudhury, L. H.; S. Ghosh, *J. Mol. Catal. A: Chem.* **2006**, *255*, 230-235.
48. Ziyaei, A.; Azizi, N.; Saidi, M. R. *J. Mol. Catal. A: Chem.* **2005**, *238*, 138-141.
49. Kumar, R.; Thilagavathi, R.; Gulhane, R.; Chakraborti, A. K. *J. Mol. Catal. A: Chem.* **2006**, *250*, 226-231.
50. Hajipour, A. A.; Khazdooz, L.; Ruoho, A. E. *Catal. Commun.***2008**, *9*, 89-96.
51. Setamdideh, D.; Khezri, B.; Esmailzadeh, S. *J. Chin. Chem. Soc.* **2012**, *59*, 1119-1124.
52. Setamdideh, D.; Khezri, B.; Alipouramjad, A. *J. Chin. Chem. Soc.* **2013**, *60*, 590-596.
53. Sofighaderi, S.; Setamdideh, D. *Orient. J. Chem.* **2013**, *29*, 1135-1137.
54. Setamdideh, D.; Sepehraddin, F. *J. Mex. Chem. Soc.* **2014**, *58*, 22-26.
55. Setamdideh, D.; Khezri, B.; Rahmatollahzadeh, M.; Alipouramjad, A. *Asian J. Chem.***2012**, *8*, 3591-3596.
56. Setamdideh, D.; Rahmatollahzadeh, M. *J. Mex. Chem. Soc.* **2012**, *56*, 169-175.
57. Kamari, R.; Setamdideh, D. *Orient. J. Chem.***2013**, *29*, 497-499.
58. AziziAsl, P.; Setamdideh, D. *J. Chin. Chem. Soc.* **2014**, *61*, 940-944.
59. Setamdideh, D. *J. Mex. Chem. Soc.* **2014**, *58*, 230-234.