

This article was downloaded by:[CDL Journals Account]
[CDL Journals Account]

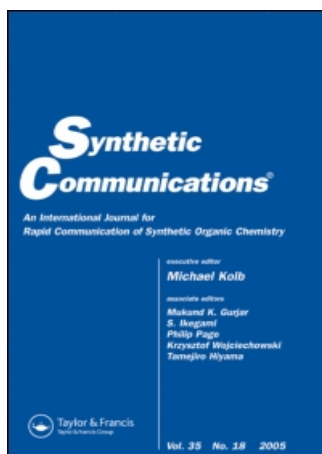
On: 12 April 2007

Access Details: [subscription number 770849124]

Publisher: Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954

Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Synthetic Communications

An International Journal for Rapid
Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title-content=t713597304>

An Efficient and Convenient Procedure for Preparation of 1,1-Diacetates from Aldehydes Catalysed by Expansive Graphite

Tong-Shou Jin ^a; Gui-Ying Du ^a; Zhan-Hui Zhang ^a; Tong-Shuang Li ^a

^a Department of Chemistry, Hebei University. Baoding, Hebei Province, 071002.
P.R.China

To cite this Article: Tong-Shou Jin, Gui-Ying Du, Zhan-Hui Zhang and
Tong-Shuang Li, 'An Efficient and Convenient Procedure for Preparation of

1,1-Diacetates from Aldehydes Catalysed by Expansive Graphite', Synthetic Communications, 27:13, 2261 - 2266

To link to this article: DOI: 10.1080/00397919708003380

URL: <http://dx.doi.org/10.1080/00397919708003380>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article maybe used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

© Taylor and Francis 2007

AN EFFICIENT AND CONVENIENT PROCEDURE FOR PREPARATION OF 1,1-DIACETATES FROM ALDEHYDES CATALYSED BY EXPANSIVE GRAPHITE

Tong-Shou Jin, Gui-Ying Du, Zhan-Hui Zhang and Tong-Shuang Li*

Department of Chemistry, Hebei University, Baoding 071002, Hebei Province,
P.R.China.

Abstract: An easy preparation of 1,1-diacetates from aldehydes has been carried out in excellent yield under catalysis of expansive graphite at room temperature.

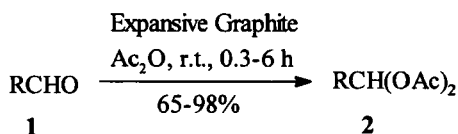
1,1-Diacetates are synthetically useful as protecting group for aldehydes^[1] due to their moderate stability and easy conversion into parent aldehydes.^[2-6] They are also important starting materials for synthesis of valuable intermediates of Diels-Alder cycloaddition reactions.^[7]

In the conventional methods, the synthesis of 1,1-diacetates were carried out under catalysis of strong proton acids such as sulphuric acid, phosphoric acid or methanesulphonic acid^[8] and Lewis acids, such as zinc chloride.^[9] These methods

* To whom correspondence should be addressed

have not been entirely satisfactory, owing to such drawbacks as low yields, long reaction time, emerging the problems of corrosivity, tedious workup and effluent pollution. In recent years, several groups have tried to improve yields, decrease reaction time and eliminate above unfavorable effects. Michie and Miller^[10] employed phosphorus trichloride as catalyst to give good yields for most of aldehydes, but reaction time ranging from 1 to 120 h and the yields are poor for aromatic aldehydes containing electron-withdrawing groups. Olah and Mehrotra succeeded in reducing the reaction time ranging from 1 to 18 h catalysed by Nafion-H.^[11] Kochhar *et al* developed a fast reaction (less than 30 min) even for α,β -unsaturated aldehydes and aromatic aldehydes having electron-withdrawing groups by using ferric chloride.^[6] More recently, Y-zeolite,^[12] β -zeolite,^[13] sulfated zirconia,^[14] HZSM-5 and tungstosilicic acid^[15] and montmorillonite clays^[16] were applied as catalysts for this purpose to obtain relatively better results.



Expansive graphite have been used as efficient catalysts for a variety of organic reactions.^[17-20] Herein we wish to report an easy and efficient procedure for the synthesis of 1,1-diacetates from aldehydes catalysed by expansive graphite.



As shown in Table, a series of 1,1-diacetates(**2**) were synthesized under catalysis of expansive graphite at room temperature. Both aromatic and aliphatic aldehydes gave good to excellent yield of the corresponding 1,1-diacetates. For example, furfural gave 2-furanylmethanediol diacetate(**2n**) in 82% yield and chloral diacetate(**2b**) was obtained in 65% yield by distillation. *p*-Nitrobenzaldehyde

required relatively longer reaction time(6 h) possibly due to the strong electron-withdrawing nitro group.

Table. Conversion of Aldehydes into 1,1-Diacetates in the Presence of Expansive Graphite

Aldehyde (1) R	Diacetate (2) R	Solvent /Time(h)	Isolated Yield(%)	bp/Torr or mp (°C)	
				found	reported
Et (1a)	Et (2a)	none/1	85	120-124/30	115-118/8 ^[6]
Cl ₃ CCH(OH) ₂ (1b)	Cl ₃ C (2b)	none/4	65	140-143/30	98-99/6 ^[21]
C ₆ H ₅ (1c)	C ₆ H ₅ (2c)	none/0.5	96	45-46	44-46 ^[10]
4-CH ₃ C ₆ H ₄ (1d)	4-CH ₃ C ₆ H ₄ (2d)	none/0.4	98	81-82	78-80 ^[6]
4-MeOC ₆ H ₄ (1e)	4-MeOC ₆ H ₄ (2e)	none/0.3	98 ^a	64-65	64-65 ^[8]
4-ClC ₆ H ₄ (1f)	4-ClC ₆ H ₄ (2f)	CCl ₄ /1	97	81-82	79-80 ^[8]
3-ClC ₆ H ₄ (1g)	3-ClC ₆ H ₄ (2g)	none/1	95 ^a	65-66	65-66 ^[8]
4-O ₂ NC ₆ H ₄ (1h)	4-O ₂ NC ₆ H ₄ (2h)	CCl ₄ /6	93	125-126	124-125 ^[8]
3-O ₂ NC ₆ H ₄ (1i)	3-O ₂ NC ₆ H ₄ (2i)	CCl ₄ /4	94	65-66	63-64 ^[8]
2-HOC ₆ H ₄ (1j)	2-AcOC ₆ H ₄ (2j)	none/2	94 ^a	105-106	104-105 ^[22]
Ph  (1k)	Ph  (2k)	none/1	97 ^a	84-85	84-87 ^[10]
2-furyl (1l)	2-furyl (2l)	none/3	82	51-53	52-54 ^[12]
3-MeO-4-HOC ₆ H ₃ (1m)	3-MeO-4-AcOC ₆ H ₃ (2m)	CCl ₄ /2	93 ^a	90-91	79-80 ^[8]
3,4-(OCH ₂ O)C ₆ H ₃ (1n)	3,4-(OCH ₂ O)C ₆ H ₃ (2n)	CCl ₄ /1	98 ^a	79-80	75-76 ^[8]

^a Satisfactory elemental analysis obtained: C \pm 0.20, H \pm 0.19.

Mention must be made here that phenol groups were also protected as acetates in hydroxyl containing aromatic aldehydes(1j and 1m). It is also worth noting that ketones, such as cyclohexanone and acetophenone, were not acetylated under these conditions. Therefore the present procedure is a selective preparation of 1,1-diacetates of aldehydes in the presence of ketones. We also tried the reaction of

maleic anhydride, phthalic anhydride and succinic anhydride with benzaldehyde in the catalysis expansive graphite. However, none of these reagents gave the corresponding cyclic diesters even the reaction mixtures were stirred at r.t. for 2 days and the materials were recovered quantitatively.

In conclusion, we provide an alternative tool for the preparation of 1,1-diacetates from aldehydes, because of its operational simplicity, high yields, short reaction time and minimal environment impact.

Experimental

Boiling and melting points were uncorrected. The products were characterized by their melting or boiling points or/and IR, ^1H NMR and mass spectra and comparison with literature values.

Preparation of expansive graphite

A mixture of concentrated sulfuric acid (98%, 20 g), nitric acid (65%, 10 g), natural flake graphite (10 g) and potassium permanganate (0.7 g) was stirred at r.t. for 30 min. The expansive graphite was filtered, washed with water until $\text{PH}=6\sim7$ and dried at $60\text{ }^\circ\text{C}$ for 1 h.

General procedure for the preparatin of 1,1-diacetates(2)

A mixture of the aldehyde (1, 10 mmol), acetic anhydride (30 mmol) and expansive graphite (200 mg) was stirred at room temperature for the length of time indicated in Table. For the reactions with solvent CCl_4 (5 mL) was also added. The progress of the reaction was monitored by TLC. After completion, Et_2O (10 mL) was added to the reaction mixture and the expansive graphite was filtered off. The catalyst was washed with Et_2O (2 x 10 mL) and then the filtrate

was washed with 5% HCl (20 mL), 5% NaHCO₃ and brine (2 x 20 mL) successively and dried (MgSO₄). The solvent was removed under reduced pressure and the residue was purified by distillation or crystallization from cyclohexane.

Acknowledgements: The project was supported by National Natural Science Foundation of China, Education Commission of Hebei Province and Science and Technology Commission of Hebei Province.

References

- [1] Green, T. W. and Wuts, P. G. M. "Protective Groups in Organic Synthesis," 2nd Ed., John Wiley, New York, **1991**, pp. 175-223.
- [2] Perez, E. R.; Marrero, A. L.; Perez, R. and Autie, M. A. *Tetrahedron Lett.* **1995**, *36*, 1779.
- [3] Cotellet, P. and Catteau, J.-P. *Tetrahedron Lett.* **1992**, *33*, 3855.
- [4] Varma, R. S.; Chatterjee, A. K. and Varma, M. *Tetrahedron Lett.* **1993**, *34*, 3207.
- [5] Ku, Y. Y.; Patel, R. and Sawick, D. *Tetrahedron Lett.* **1993**, *34*, 8037.
- [6] Kochhar, K. S.; Bal, B. S.; Deshpande, R. P.; Rajadhyaksha, S. N. and Pinnick, H. W. *J. Org. Chem.* **1983**, *48*, 1765.
- [7] Snider, B. B. and Amin, S. G. *Synth. Commun.* **1978**, *8*, 117.
- [8] Freeman, F. and Karcherski, E. M. *J. Chem. Eng. Data* **1977**, *22*, 355.
- [9] Scriabine, I. *Bull. Soc. Chim. Fr.* **1961**, 1194.
- [10] Michie, J. K. and Miller, J. A. *Synthesis* **1981**, 824.
- [11] Olah, G. A. and Mehrotra, A. K. *Synthesis* **1982**, 962.
- [12] Pereira, C.; Cigante, B.; Marcelo-Curto, M. J.; Carreyre, H.; Perot, G. and Guisnet, M. *Synthesis* **1995**, 1077.

- [13] Kumar, P.; Hegda, V. R. and Kumar, T. P. *Tetrahedron lett.* **1995**, 36, 601.
- [14] Raju, S. V. N. *J. Chem. Research(S)* **1996**, 68.
- [15] Joshi, M. V. and Narasimbam, C. S. *J. Catal.* **1993**, 141, 308.
- [16] Zhang, Z.-H.; Li, T.-S. and Fu, C.-G. submitted to *J. Chem. Research(S)*.
- [17] Susumu, T.; Kenji, F.; Tadashi, M.; Yoshihisa, S. and Hayao, L. *Bull. Chem. Soc. Jpn.* **1991**, 64, 1011.
- [18] Susumu, T.; Kenji, F.; Yoshihisa, S. and Hayao, L. *Chem. Express* **1989**, 4, 633. *Chem. Abstr.* **1990**, 112, 97834s.
- [19] Podberezine, A. S.; Novikov, Yu. N.; Kheifits, L. A. and Volpin, M. E. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1984**, 1907. *Chem. Abstr.* **1984**, 101, 210658a.
- [20] Bertin, J.; Kagan, H. B.; Luche, J.-L. and Setton, R. *J. Am. Chem. Soc.* **1974**, 96, 8113.
- [21] Vulfson, N. S. *Zh. Obshch. Khim.* **1950**, 20, 595; *Chem. Abstr.* **1951**, 45, 557b.
- [22] Hisashi, I. and Seisuke, T. *J. Pharm. Soc. Japan.* **1952**, 72, 876; *Chem. Abstr.* **1953**, 47, 6413b.

(Received in the UK 29th November 1996)