

TiO₂/SO₄²⁻, a convenient and efficient catalyst for desilylation-acetylation of trimethylsilyl ethers with acetic anhydride†

Tong-Shou Jin*, Yan-Wei Li, Guang Sun and Tong-Shuang Li

Department of Chemistry, College of Chemistry and Environmental Science, Hebei University, Baoding 071002, P. R. China

A rapid method for desilylation-acetylation of trimethylsilyl ethers with acetic anhydride catalysed by TiO₂/SO₄²⁻ at room temperature is reported.

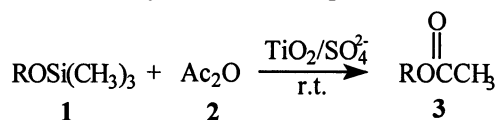
Keywords: TiO₂/SO₄²⁻, desilylation, acetylation, trimethylsilyl ethers, acetic anhydride

Carboxylic esters have been extensively used in industry and commerce. They are synthesised by many methods. For example, esterification of carboxylic acids and alcohols,¹ transesterification,² alkylation of carboxylate anions³ and acylation of alcohols or phenols.^{4,5} On the other hand, ethers are also changed into esters by acylation using acylating agents such as acyl and aroyl halides (including sulfonyl halides) and anhydrides of carboxylic acids.^{6,7} Ganem and small⁷ reported a dual mechanism involving O-acylation of the ether followed by dissociation to the more stable carbonium ion or nucleophilic displacement (S_N1 or S_N2) at the oxonium by acetate.

Trimethylsilyl (TMS) ethers can be converted into the corresponding acetates using acetyl chloride and zinc chloride in acetonitrile⁸ and acetic anhydride and montmorillonite K-10.⁹ These methods have their merits and some shortcomings. Some methods have not been entirely satisfactory with drawbacks such as long reaction times (up to 24 h in the case of α -naphthyl trimethylsilyl ether),⁹ low yields, tedious work-up, the emerging problem of corrosivity, effluent pollution and expensive, non-recoverable and unavailable catalysts.

In recent years, solid superacids have been used as efficient catalysts for a variety of organic reactions.¹⁰⁻¹⁵ TiO₂/SO₄²⁻, a kind of solid superacid, has been extensively used in organic synthesis¹⁰⁻¹³ due to its strong acidity, inexpensiveness, non-corrosive nature, reusability and non-polluting nature. The reaction catalysed by TiO₂/SO₄²⁻ is usually carried out under mild conditions with high yield and selectivity. The work-up of the reactions is very simple; usually only removal of the catalyst by filtration and evaporation of the solvent are involved. In connection with our ongoing work on TiO₂/SO₄²⁻, we report herein the desilylation-acetylation of trimethylsilyl ethers with acetic anhydride catalysed by TiO₂/SO₄²⁻ (Scheme 1).

In the presence of TiO₂/SO₄²⁻, treatment of a variety of silylated alcohols or phenols (**1**) with acetic anhydride (**2**) in dichloromethane (except for those in absence of solvent) at room temperature gave the corresponding acetates (**3**) in good yields. The results are shown in Table 1. The present procedure gives relatively better yields and needs much shorter reaction times than the reaction with a montmorillonite K-10 catalyst⁹. For example, α -naphthyl acetate (**3k**) was obtained in 32% yield with montmorillonite K-10 catalyst after 24 hours at room temperature. However, our procedure with a TiO₂/SO₄²⁻ catalyst after only 35 minutes gave α -naphthyl acetate (**3k**) in 78% yield at room temperature.



Scheme 1

*To receive any correspondence. E-mail orgsyn@mail.hbu.edu.cn

†This is a Short Paper, there is therefore no corresponding material in J. Chem. Research (M).

In conclusion, we have developed a desilylation-acetylation reaction of trimethylsilyl ethers with the advantages of operational simplicity, high yields, short reaction times and a recyclable and environmentally-friendly catalyst.

Experimental

Trimethylsilyl ethers were synthesised as described in ref. 22. The catalyst TiO₂/SO₄²⁻ solid superacid was prepared as follows: Ti(OH)₄ was obtained by hydrolysing TiCl₄ with aqueous ammonium hydroxide, washing the precipitates with deionized water until chloride was absent, drying them at 120°C for 4h, and powdering the precipitates below a 100 mesh. The hydroxide was treated with 1M H₂SO₄ for 4h, then filtered off, dried by calcining in a furnace at 450–500°C for 4h and finally stored in a desiccator until use. Acid centres are formed which result in an acid strength H₀ ≤ -14.57 (Fig. 1).

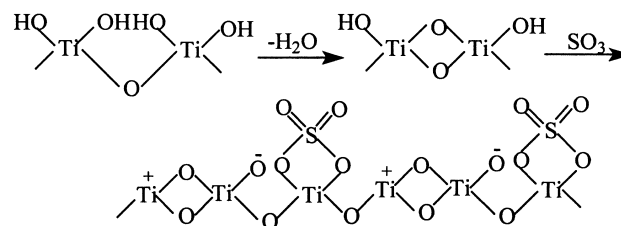


Fig. 1

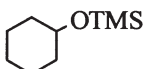
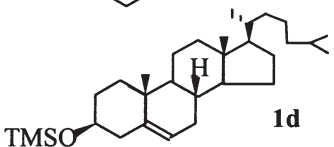
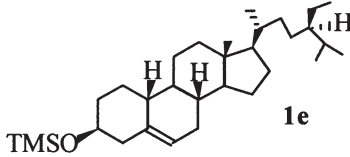
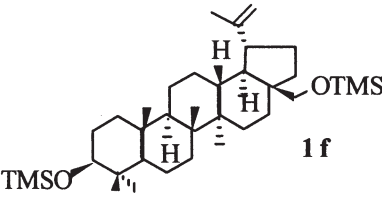

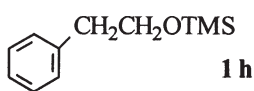
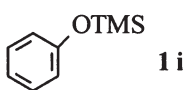
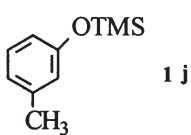
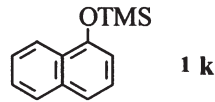
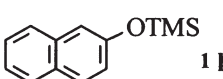
General procedure for conversion of the trimethylsilyl ethers into the corresponding acetates (3): A mixture of the trimethylsilyl ether (1mmol) and acetic anhydride (5mmol) in dry dichloromethane (5ml) (except for those in absence of solvent) was stirred in the presence of TiO₂/SO₄²⁻ (250mg) at room temperature for the length of time as indicated in Table 1. The reaction was monitored by TLC. After completion of the reaction, the mixture was filtered and the catalyst was washed with dichloromethane (2 × 5ml). The filtrate was washed with saturated aqueous NaHCO₃ (2 × 15ml) and brine (2 × 10ml) and dried over anhydrous Na₂SO₄. Removal of the solvent under reduced pressure furnished the essentially pure product (**3**). Further purification was achieved by column chromatography on silica gel using petroleum ether and diethyl ether as eluent. All products were characterised by their melting points or boiling points, spectral characteristics (IR and ¹H NMR) and comparison with authentic samples. ¹H NMR spectra were determined in D-chloroform or tetrachloromethane solution on a FT-NMR Bruker 400 (400MHz), and reported in δ ppm using tetramethylsilane as the standard.

3d: m.p. 112–114°C (lit 114–115°C¹⁸) (colourless needles from acetone); ¹H NMR (CDCl₃): δ_{H} 5.39 (1H, d, $J=4.4$ Hz, 6-H), 4.64 (1H, m, 3 α -H), 1.04 (3H, s, 19-Me), 0.94 (3H, d, $J=6.4$ Hz, 21-Me), 0.88 (6H, d, $J=6.4$ Hz, 26, 27-Me), 0.70 (3H, s, 18-Me), 2.05 (3H, s, 3-OCOCH₃).

3f: m.p. 222–224°C (lit 218–220°C²⁰) (colourless needles from acetone); ¹H NMR (CDCl₃): δ_{H} 4.71 (1H, s, 29-H), 4.61 (1H, s, 29-H'), 4.27 (1H, d, $J=11.2$ Hz, 28-H), 3.87 (1H, d, $J=11.2$ Hz, 28-H'), 2.32 (1H, m, 3-H), 1.66–1.08 (complex, CH₂, CH), 1.70 (3H, s, 30-Me), 1.41, 1.05, 0.99, 0.87, 0.85 (15H, all s, 5 × Me), 2.09 (3H, s, 3-OCOCH₃), 2.06 (3H, s, 22-OCOCH₃).

3h: n_{D}^{20} 1.4990; ¹H NMR (CCl₄): δ_{H} 1.90 (3H, s, 1-OCOCH₃), 2.81 (2H, t, $J=7$ Hz, 2-CH₂), 4.14 (2H, t, $J=7$ Hz, 1-CH₂), 7.11 (5H, s, 2-C₆H₅).

Table 1 Desilylation-acetylation of trimethylsilyl ethers with acetic anhydride catalyzed by $\text{TiO}_2/\text{SO}_4^{2-}$

Entry	Substrate	Solvent	Time /min	Yield/% ^a	B.p./torr or m.p./ °C Found	°C Reported
1	$\text{CH}_3(\text{CH}_2)_6\text{OTMS}$ 1a	None	12	80	90–92/30	192.5/760 ¹⁶
2	$\text{CH}_3(\text{CH}_2)_8\text{CH}_2\text{OTMS}$ 1b	None	15	85	132–134/20	244/760 ¹⁷
3	 1c	None	20	60	80–82/30	173/760 ¹⁷
4	 1d	CH_2Cl_2	25	77	112–114	114–115 ¹⁸
5	 1e	CH_2Cl_2	50	34	120–122	120.5–122 ¹⁹
6	 1f	CH_2Cl_2	80	50 ^b	222–224	218–220 ²⁰
7	 1g	None	8	89	115–117/25	215.5/760 ¹⁷
8	 1h	None	12	84	122–124/20	232.6/760 ²¹
9	 1i	None	30	85	100–102/30	196/760 ²¹
10	 1j	None	25	68	112–114/25	212/760 ¹⁷
11	 1k	None	35	78	42–44	43–46 ²¹
12	 1l	None	55	68	70–72	69–70 ²¹

^aYields refer to isolated products.^bYield refer to diacetylated product.

The project was supported by the National Natural Science Foundation of China (29872011 and 29572039), the Educational Ministry of China, the Educational Department of Hebei Province (990104) and the Science and Technology Commission of Hebei Province.

Received 17 June 2002; accepted 2 September 2002
Paper 02/1426

References

- 1 E. Haslam, *Tetrahedron*, 1980, **36**, 2409 and references cited therein.
- 2 A. Loupy, A. Petit, M. Ramdani and C. Yvanaeff, *Can. J. Chem.*, 1993, **71**, 90.
- 3 G. Bram, A. Loupy and M. Majdoub, *Synth. Commun.*, 1990, **20**, 125; G. Bram, A. Loupy, M. Majdoub, E. Gutierrez and E. Ruiz-Hitzky, *Tetrahedron*, 1990, **46**, 5167.
- 4 R.I. Zhdanov and S.M. Zhenodarova, *Synthesis*, 1975, 222.
- 5 K. Ishihara, M. Kubota, H. Kurihara and H. Yamamoto, *J. Org. Chem.*, 1996, **61**, 4560.
- 6 R.L. Burwell, *Chem. Rev.*, 1954, **54**, 615 and references cited therein.
- 7 B. Ganem and V.R. Small, *J. Org. Chem.*, 1974, **39**, 3728.
- 8 S. Kim and W.J. Lee, *Synth. Commun.*, 1986, **16**, 659.
- 9 B. Movassagh, M.M. Lakouraj and J. Fasihi, *J. Chem. Res. (S)*, 2000, 348.
- 10 T.S. Jin, Y.R. Ma, X. Sun, D. Liang and T.S. Li, *J. Chem. Research (s)*, 2000, 96.
- 11 T. S. Jin, X. Sun and T.S. Li, *J. Chem. Research (S)*, 2000, 128.
- 12 T. S. Jin, Y.R. Ma, Y. Li, X. Sun and T.S. Li, *Synth. Commun.*, 2001, **31**, 111.
- 13 X. Sun, X.F. Wang, T.S. Jin and T.S. Li, *Chin. J. Hebei University*, 2001, **21**, 49.
- 14 J.J. Guo, T.S. Jin and T.S. Li, *Chin. Chemical World* 2002, **43**, 85.
- 15 T.S. Jin, S.L. Zhang, X.F. Wang, J.J. Guo and T.S. Li *J. Chem. Research (S)*, 2001, 289.
- 16 E.E. Royals, *J. Org. Chem.*, 1958, **23**, 1822.
- 17 R.C. Weast and M.J. Astle, *CRC Handbook of Data on Organic Compounds*, Vol. 2, 2nd edn. CRC Press Inc., Boca Raton Florida, 1985.
- 18 J. Buckingham and S.M. Donghy, "Dictionary of Organic Compounds," 5th edn., Chapman and Hall New York, London Toronto, 1982.
- 19 U. Wrzeczono, *Roczniki Chem.*, 1965, **39**, 385.
- 20 R.S. Ludwiczak and K. Szczawinska, *Roczniki Chem.*, 1965, **39**, 583.
- 21 R. Maris, J. Nagorkatti, J. Heaton and C. Lane, *Aldrich Catalog Handbook of Fine Chemicals*, 1001 West Saint Paul Avenue, Milwaukee, WI 53233, USA, 1996–1997.
- 22 Z.H. Zhang, T.S. Li, F. Yang and C.G. Fu, *Synth. Commun.*, 1998, **28**, 3105