This article was downloaded by: [UQ Library]
On: 07 November 2014, At: 09:46
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

Organic Preparations and Procedures International: The New Journal for Organic Synthesis
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/uopp20

TETRAHYDROFURAN RING-OPENING WITH ACID ANHYDRIDES CATALYZED BY SAMARIUM TRIIODIDE

Weiliang Bao [a] , Taokai Ying [a] , Yongmin Zhang [a] & Mingxin Yu [a]
[a] Department of Chemistry , Hangzhou University Hangzhou , Zhejiang, 310028, PR CHINA

Published online: 09 Feb 2009.

To cite this article: Weiliang Bao , Taokai Ying , Yongmin Zhang & Mingxin Yu (1997) TETRAHYDROFURAN RING-OPENING WITH ACID ANHYDRIDES CATALYZED BY SAMARIUM TRIIODIDE, Organic Preparations and Procedures International: The New Journal for Organic Synthesis, 29:3, 335-337, DOI: 10.1080/00304949709355207

To link to this article: http://dx.doi.org/10.1080/00304949709355207

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the “Content”) contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions

4. H. Tecle, D. J. Lauffer, R. E. Davis, T. Mirzadegan, D. W. Moreland, R. D. Schwarz, A. J. Thomas, C. Raby, D. Eubanks, M. R. Brann and J. C. Jaen, *ibid.*, **5**, 637 (1995).

5. J. Jaen, S. Barrett, M. Brann, M. Callahan, R. Davis, P. Doyle, D. Eubanks, D. Lauffer, L. Lauffer, W. Lipinski, D. Moreland, C. Nelson, C. Raby, R. Schwarz, C. Spencer and H. Tecle, *Life Sciences*, **55**, 845 (1995).

6. D. O. Spry and H. S. Aaron, *J. Org. Chem.*, **34**, 3674 (1969).

7. K. Hasse and A. Wieland, *Chem. Ber.*, **93**, 1686 (1960).

8. O. Mitsunobu, *Synthesis*, 1 (**1981**). Hughes [D. L. Hughes, *Org. Prep. Proced. Int.*, **28**, 127 (1996)] has written a recent review of the progress in the Mitsunobu reaction.

9. R. C. Bernotas and R. V. Cube, *Tetrahedron Lett.*, **32**, 161 (1991).

10. J. Boelsterli, U. Eggnauer, E. Pombo-Villar, H. Weber, M. Walkinshaw and R. O. Gould, *Helv. Chim. Acta*, **70**, 1065 (1987).

11. V. M. Micovic and M. L. Mihailovic, *J. Org. Chem.*, **18**, 1190 (1953).

****

TETRAHYDROFURAN RING-OPENING WITH ACID ANHYDRIDES CATALYZED BY SAMARIUM TRIIODIDE

Submitted by
(06/05/96)

Weiliang Bao, Taokai Ying, Yongmin Zhang* and Mingxin Yu

Department of Chemistry, Hangzhou University
Hangzhou, Zhejiang 310028, P. R. CHINA

The application of lanthanide compounds to organic synthesis has recently emerged as a valuable synthetic method.[1] Some lanthanide compounds such as $CeCl_3$ and SmI_2 have gained much attention and have become versatile reagents in organic synthesis.[2] However, liftte attention has been paid to the use of samarium(III) compounds. We reported that samarium triiodide catalyzes the formation of dithioacetals and dithioketals[3] and carbon-carbon double bonds between α-halo ketones and aldehydes.[4] More recently we have also found that tetrahydrofuran ring opening with acid chlorides is promoted by SmI_3.[5] We now report that tetrahydrofuran can be opened with cyclic and acyclic anhydrides in the presence of a catalytic amount of samarium triiodide under mild conditions to give the corresponding 4-iodobutyl esters.

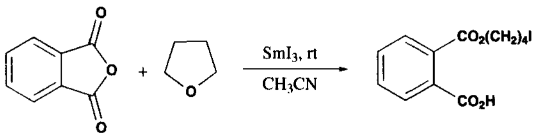
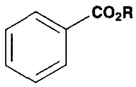
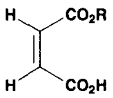
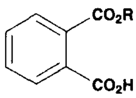


TABLE. Yield, mp. and Spectral Data of 4-Iodobutyl Esters

Product R = $(CH_2)_4I$	Yield (%)	Time (hrs)	bp. (°C)	Anal. Calcd (Found) C	H	^{1}H NMR (δ)	IR (cm^{-1})
CH_3CO_2R	90	2	228-229[a]			1.95 (s, 3H) 1.66-2.00 (m, 4H) 3.06-3.27 (t, 2H) 3.90-4.10 (t, 2H)	2980, 1753, 1373, 1242, 1040, 600
$C_2H_5CO_2R$	87	2	233-234	32.83 (33.01)	5.12 (5.27)	1.00-1.23 (t, 3H) 1.66-2.00 (m, 4H) 2.09-2.46 (q, 2H) 3.10-3.31 (t, 2H) 3.94-4.13 (t, 2H)	2980, 2960, 1750, 1470, 1355, 1085
n-$C_3H_7CO_2R$	92	2	240-241	35.57 (35.79)	5.60 (5.53)	0.87-2.36 (m, 11H) 3.10-3.32 (t, 2H) 3.96-4.15 (t, 2H)	2980, 2890, 1750, 1470, 1360, 1090
n-$C_5H_{11}CO_2R$	81	2	244-245	40.28 (40.05)	6.42 (6.40)	0.87-2.33 (m, 15H) 3.07-3.27 (t, 2H) 3.93-4.1 3 (t, 2H)	2970, 2950, 2890, 2875, 1750, 1470, 1230, 1170, 1100
	73	3	287 (dec.)	43.44 (43.59)	4.31 (4.27)	1.80-2.02 (m, 4H) 3.10-3.30 (t, 2H) 4.17-4.36 (t, 3H) 7.33-8.05 (m, 5H)	3080, 3055, 2980, 2920, 1735, 1725, 1612, 1595, 1460, 1320, 1280, 1180, 1115, 1070, 705
	62	3	269 (dec.)	32.24 (32.49)	3.72 (3.68)	1.73-1.97 (m, 4H) 3.09-3.29 (t, 2H) 4.12-4.30 (t, 2H) 6.30 (s, 2H) 10.23 (s, 1 H)	3080, 2980, 1752, 1745, 1738, 1720, 1655, 1645, 1435, 1230, 1170, 785
	58	3	298 (dec.)	41.40 (41.49)	3.76 (3.68)	1.76-2.03 (m, 4H) 3.13-3.32 (t, 2H) 4.25-4.43 (t, 2H) 7.50-8.00 (m, 4H) 10.17 (s, 1H)	3350, 3100, 2980, 2890, 1740, 1700, 1610, 1590, 1500, 1420, 1170, 740

a) Lit.[6] 92-95°/1.5mmHg.

Compared to the sodium iodide-acyl chloride system, the title reaction proceeds in shorter time and gives higher yields.[6] The simple conditions used in this work are even milder than those of the previously reported reaction with acid chlorides, because anhydrides are easier to purify and handle than acid chlorides.[5] 4-iodobutyl phthalate and 4-iodobutyl maleate are new compounds. This reaction provides a new method for the synthesis of this class of compounds in high yield.

EXPERIMENTAL SECTION

^{1}H NMR spectra were recorded in CCl_4 on a JEOL PMX 60si spectrometer using TMS as internal standard. IR spectra were obtained on a Perkin-Elmer 683 instrument. Tetrahydrofuran was freshly distilled from sodium/benzophenone ketyl prior to use. The anhydrides were purified to remove any acid.[7] All the reactions were carried out under a nitrogen atmosphere.

General Procedure.- Samarium powder (0.3g, 2 mmol) was placed in a three-necked round bottom flask with a magnetic stir bar. The flask was flushed with nitrogen several times. Acetonitrile (20 mL) and then iodine *(0.75g,* 6 mmol) were added. After the mixture had been stirred for 30 min., tetrahydrofuran (8 mmol) and the acid anhydride (8 mmol) were added. The resulting solution was stirred for the specified time and then the solvent was evaporated under vacuum. The residue was extracted with ether (2 x 30 mL), washed with saturated aqueous NaCl solution (15 mL), $Na_2S_2O_3$ solution (15 mL) and then NaCl solution (15 mL), and dried over $MgSO_4$. After filtration and removal of the solvent, the crude product was purified by column chromatography (silica gel) using cyclohexane/ethyl acetate as eluent.

Acknowledgment.- This work was supported by the National Science Foundation of China.

REFERENCES

1. a) H. B. Kagan and J. L. Namy, *Tetrahedron*, **42**, 6573 (1986); b) J. Inanaga, *Yuki Gosci Kagaku KyokaiShi (Japan)*, **47**,200 (1989); *Chem. Abstr.*, **110**, 191874k (1989).
2. G. A. Molander, *Chem. Rev.*, **92**, 29 (1992).
3. Y. Zhang, Y. Yu and R. Lin, *Org. Prep. Proced. Int.*, **25**, 365 (1993).
4. Y. Zhang, Y. Yu and R. Lin, *Tetrahearon Lett.*, **34**, 4547(1993).
5. Y. Yu, Y. Zhang and R. Lin, *Synth.Commun.*, **23**, 1973 (1993).
6. A. Oku, T. Harada and K. Kita, *Tetrahearon Lett.*, **23**, 681 (1982).
7. D. D. Perrin, W. F. Armarego and D. R. Perrin, *"Purification of Laboratory Chemicals"*, 2nd Ed., p. 554, Pergamon Press, Oxford, 1980.

****