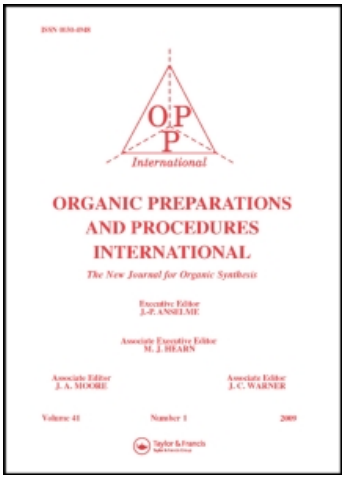

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TETRAHYDROFURAN RING-OPENING WITH ACYLOXYPHOSPHONIUM IODIDE CATALYZED BY SAMARIUM TRIIODIDE

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6. M. Narita and C. U. Pittman Jr., *Synthesis*, 489 (**1976**).

7. N. F. Haley and M. W. Fichtner, *J. Org. Chem.*, **45**, 2959 (1980).

8. N. F. Haley and M. W. Fichtner, *ibid.*, **45**, 175 (1980).

9. I. Degani and R. Fochi, *Synthesis*, 263 (**1977**).

10. E. Campaigne and F. Haaf, *J. Org. Chem.*, **30**, 732 (1965).

11. H. D. Hartzler, *J. Am. Chem. Soc.*, **95**, 4379 (1973).

12. J. Nakayama, *Synthesis*, 38 (**1975**).

13. K. Clausen, A. A. El-Barbary and S. O. Lawesson, *Tetrahedron*, **37**, 1019 (1981).

14. G. Adiwidjaja, H. Gunther and J. Voss, *Angew. Chem. Int. Ed. Engl.*, **19**, 563 (1980).

15. G. Adiwidjaja, H. Gunther and J. Vob, *Ann.*, 1116 (**1983**).

16. D. W. Francoise, R. Merenyi, H. G. Viehe, *Synthesis*, 79 (**1985**).

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TETRAHYDROFURAN RING-OPENING WITH ACYLOXYPHOSPHONIUM IODIDE CATALYZED BY SAMARIUM TRIIODIDE

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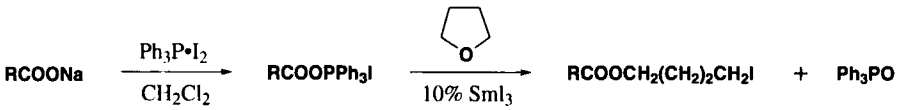
Tetrahydrofuran ring opening with acyl halides or acid anhydrides is a useful method for preparation of 4-halobutyl esters.[1] Several methods have been reported for this purpose, e.g. the reaction of tetrahydrofuran with sodium iodide and acid chlorides,[2] the tetrahydrofuran ring–opening with acid chlorides or acid anhydrides catalyzed by samarium triiodide[3,4] to give 4-iodobutyl esters; the

acylative ring-opening of tetrahydrofuran with acid chlorides catalyzed by yttrium trichloride[5], titanium chloride or stannic chloride[6] to produce 4-chlorobutyl esters, etc. However, all of these procedures are restricted to use acyl chlorides or acid anhydrides, which are not easy to prepare, handle and purify, as the acylating reagents. Furthermore, some of these methods suffer from long reaction time,[2,5,6] thermal conditions[5,6] (under reflux), or low yields.[4] Thus, there is still considerable interest in finding more convenient and effective methods for the synthesis of 4-halobutyl esters.

Over the last decades, acyloxyphosphonium salts have been reported as a new type of acylating agent. Such species could be generated *in situ* by treatment of a mixture of a carboxylic acid and triphenylphosphine with tetrahalomethane,[7] NBS or NCS.[8] Their application to the synthesize of amides,[7-9] esters[10] and acyl azides[11] has been reported. However, all such reactions are not "atom-economical" since the halide anions of the acyloxyphosphonium salts are not utilized. Herein, we report that the tetrahydrofuran ring can be opened with acyloxyphisphonium iodide to yield 4-iodobutyl esters (*Scheme*).



a) R = Ph, b) R = *p*-$CH_3C_6H_4$, c) R = *p*-$CH_3OC_6H_4$, d) R = *p*-ClC_6H_4, e) R = *m*-ClC_6H_4, f) R = *p*-IC_6H_4, g) R = *p*-$NO_2C_6H_4$, h) R = (E)-PhCH=CH, i) R = CH_3

A modified procedure for the preparation of acyloxyphosphonium iodide **1** was designed by direct mixing of the sodium carboxylate, triphenylphosphine and iodine in dichloromethane in order to avoid the by-products (trihalomethane in Yamada's procedure[7] and succinimide in Frøyen's procedure[8]). When tetrahydrofuran was treated with intermediate **1** catalyzed by 10 mol% samarium triiodide, 4-iodobutyl esters were obtained in good to excellent yields. The results are summarized in the **TABLE**. Species **1** was very reactive and the opening of tetrahydrofuran catalyzed by samarium triiodide was usually complete in a short time even at room temperature. If no catalyst was used, the reaction required longer time and afforded lower yields of products (cmpd **2a**). A variety of sodium carboxylates were used in the reaction. **TABLE 1** shows that sodium salts of aromatic carboxylic acids afforded excellent yields while aliphatic acids gave lower yields (cmpd **2i**). When sodium cinnamate (E form) was used, the reaction could also afford a significant yield of product (cmpd **2h**). In the course of this process, substituents such as chloro, bromo, iodo, methyl, methoxy, or nitro groups were not affected.

In conclusion, it has been found that the tetrahydrofuran ring could be efficiently opened with acyloxyphosphonium iodide to give 4-iodobutyl esters in good to excellent yields. The notable advantages of the present procedure are its mild conditions, easy availability of starting materials, simple operation, short reaction time, atom-economy and good to excellent yields.

Table 1. Yields, Bps., Elemental Analysis and Spectral Data of Compounds **2**

Cmpd	Yield (%)	Time (hrs)	Bp. (°C)	IR (cm^{-1})	^1H NMR (δ)	Anal. Calcd C	Anal. (Found) H	MS M/z (M^+)
2a	94 (64[a])	1.2 (6[a])	286[b] (dec.)	1719 (C = O)	8.03-8.01 (2H, m, ArH), 7.53-7.40 (3H, m, ArH), 4.32 (2H, t, J = 6.2 Hz, OCH_2), 3.22 (2H, t, J = 6.5 Hz, CH_2I), 1.97-1.84 (4H, m, $(CH_2)_2$)	----	----	----
2b	95	1.2	290 (dec.)	1721 (C = O)	7.91 (2H, d, J = 8.2 Hz, ArH), 7.22 (2H, d, J = 8.2 Hz, ArH), 4.31 (2H, t, J = 6.2 Hz, OCH_2), 3.22 (2H, t, J = 6.5 Hz, CH_2I), 2.38 (3H, S, CH_3), 1.99-1.85 (4H, m, $(CH_2)_2$)	45.30 (45.19)	4.75 (4.80)	319
2c	92	1.2	292 (dec.)	1712 (C = O)	7.98 (2H, d, J = 8.8 Hz, ArH), 6.92 (2H, d, J = 8.8 Hz, ArH), 4.31 (2H, t, J = 6.2 Hz, OCH_2), 3.5 (3H, s, OCH_3), 3.25 (2H, t, J = 6.5 Hz, CH_2I), 2.00-1.86 (4H, m, $(CH_2)_2$)	43.13 (43.26)	4.52 (4.57)	334
2d[3]	92	1.2	297 (dec.)	1717 (C = O)	7.96 (2H, d, J = 8.5 Hz, ArH), 7.41 (2H, d, J = 8.5 Hz, ArH), 4.34 (2H, t, J = 6.2 Hz, OCH_2), 3.23 (2H, t, J = 6.5 Hz, CH_2I), 2.00-1.88 (4H,m, $(CH_2)_2$)	----	----	----
2e	90	2.5	294 (dec.)	1720 (C = O)	7.98-7.89 (2H, m, ArH), 7.53-7.34 (3H, m, ArH), 4.34 (2H, t, J = 6.2 Hz, OCH_2), 3.24 (2H, t, J = 6.5 Hz, CH_2I), 1.99-1.88 (4H, m, $(CH_2)_2$)	39.02 (39.14)	3.57 (3.53)	338
2f	91	1.2	280 (dec.)	1718 (C = O)	7.79 (2H, d, J = 8.5 Hz, ArH), 7.72 (2H, d, J = 8.5 Hz, ArH), 4.33 (2H, t, J = 6.2 Hz, OCH_2), 3.24 (2H, t, J = 6.5 Hz, CH_2I), 1.99-1.88 (4H, m, $(CH_2)_2$)	30.72 (30.81)	2.81 (2.78)	430
2g	93	1.2	285 (dec.)	1724 (C = O)	8.30 (2H, d, J = 9.0 Hz, ArH), 8.22 (2H, d, J = 9.0 Hz, ArH), 4.42 (2H, t, J = 6.2 Hz, OCH_2), 3.28 (2H, t, J = 6.5 Hz, CH_2I), 2.04-1.94 (4H, m, $(CH_2)_2$)	37.84 (37.72)	3.46 (3.50)	350

Table 1. Continued...

Cmpd	Yield (%)	Time (hrs)	Bp. (°C)	IR (cm^{-1})	^1H NMR (δ)	Anal. Calcd C	Anal. (Found) H	MS M/z (M^+)
2h	88	1.5	289 (dec.)	1709 (C = O) 1638 (C = C)	7.67 (1H, d, J = 16.0 Hz, ArCH =), 7.51-7.49 (2H, m, ArH), 7.39-7.34 (3H, m, ArH), 6.42 (1H d, J = 16.0 Hz, = $CHCO_2$), 4.21 (2H, t, J = 6.2 Hz, OCH_2), 3.20 (2H, t, J = 6.5 Hz, CH_2I), 1.96-1.77 (4H, m, $(CH_2)_2$)	47.29 (47.15)	4.58 (4.63)	330
2i	82	5	229-230[c]	1750 (C = O)	4.04 (2H, t, J = 6.2 Hz, OCH_2), 3.16 (2H, t, J = 6.5 Hz, CH_2I), 1.95 (3H, s, CH_3), 1.92-1.74 (4H, m, $(CH_2)_2$)	----	----	----

a) Reaction was carried out without addition of catalyst. b) *Lit.*[4] 287 (dec.). c) *Lit.*[2] 92-95°C/1.5 mmHg.

EXPERIMENTAL SECTION

The boiling points are uncorrected. Infrared spectra were recorded on a Bruker Vector 22 spectrometer as KBr pellets (cm^{-1}). ^1H NMR spectra were determined in a Bruker 400 spectrometer as $CDCl_3$ solutions. J values are in Hz. Chemical shifts are expressed in ppm downfield from internal tetramethylsilane. Mass spectra were recorded on a HP 5989B MS spectrometer. Microanalysis was carried out on a Carlo Erba EA 1110 instrument. Tetrahydrofuran (THF) was distilled from sodium-benzophenone ketyl immediately prior to use. Dichloromethane was purified and dried by the standard procedure before use. All reactions were conducted under a nitrogen atmosphere. Samarium triiodide was prepared according to reported procedure.[4] After removal of solvent under reduced pressure, the resulting solid was stored for further use.

General Procedure.- To a stirred solution of triphenylphosphine (0.26g, 1.0 mmol) and iodine (0.26g, 1mmol) in anhydrous dichloromethane (10 mL) at room temperature was added sodium carboxylate (1.0 mmol) in one portion. The color of the mixture turned to yellow after 30 min which indicated that acyloxyphosphonium iodide had been formed. Then samarium triiodide (0.053g, 0.1 mmol) and THF (1.0 mmol) were added to the suspension. The resulting mixture was further stirred for the time given in the **TABLE**. Water (5 mL) was added to quench the reaction and the mixture was extracted with diethyl ether (2 x 30 mL). The extracts were washed with saturated sodium thiosulfate (5 mL) and brine. After the solution was dried over anhydrous Na_2SO_4, the solvent was removed under reduced pressure; the residue was then purified by preparative TLC on silica gel with cyclohexane-ethyl acetate (12:1) as eluent.

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REFERENCES

1. R. L. Jr. Burwell, *Chem. Rev.*, **54**, 615 (1954).
2. A. Oku, T. Harada and K. Kita, *Tetrahedron Lett.*, **23**, 681 (1982).
3. Y. P. Yu, Y. M. Zhang and R. H. Lin, *Synth. Commun.*, **23**, 1973 (1993).
4. W. L. Bao, T. K. Ying and Y. M. Zhang, *Org. Prep. Proced. Int.*, **29**, 335 (1997).
5. C. T. Qian, A. M. Qiu, Y. Z. Huang and W. J. Chen, *J. Organomet. Chem.*, **412**, 53 (1991).
6. Y. L. Gol'dfarb and L. M. Smorgonskii, *J. Gen. Chem.(USSR.)*, **8**, 1516 (1938); *Chem. Abstr.*, **33**, 4593 (1939).
7. S. I. Yamada and Y. Takeuchi, *Tetrahedron Lett.*, 3595 (**1971**).
8. P. Frøyen, *ibid.*, **38**, 5359 (1997)
9. P. Frøyen, *Synth. Commun.*, **25**, 959 (1995).
10. P. Frøyen, *Phosphorus, Sulfur and Silicon*, **91**, 145 (1994).
11. P. Frøyen, *ibid.*, **89**, 145 (1994).