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TETRAHYDROFURAN RING-OPENING WITH ACID ANHYDRIDES CATALYZED BY SAMARIUM TRIODIDE

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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, little attention has been paid to the use of samarium(III) compounds. We reported that samarium triiodide catalyzes the formation of dithioacetals and dithioketals³ 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_2 .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.

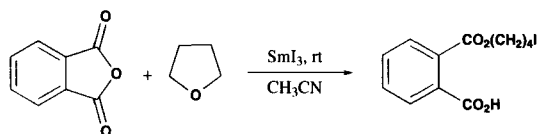
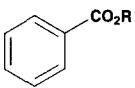
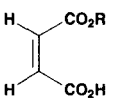
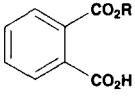


TABLE. Yield, mp. and Spectral Data of 4-Iodobutyl Esters

Product R = (CH ₂) ₄ I	Yield (%)	Time (hrs)	bp. (°C)	Anal.		¹ H NMR (δ)	IR (cm ⁻¹)
				Calcd C	(Found) H		
CH ₃ CO ₂ R	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 ₂ H ₅ CO ₂ R	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
<i>n</i> -C ₃ H ₇ CO ₂ R	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
<i>n</i> -C ₃ H ₁₁ CO ₂ R	81	2	244-245	40.28 (40.05)	6.42 (6.40)	0.87-2.33 (m, 15H) 3.07-3.27 (t, 2H) 3.93-4.13 (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, 1H)	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

¹H NMR spectra were recorded in CCl₄ 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), Na₂S₂O₃ solution (15 mL) and then NaCl solution (15 mL), and dried over MgSO₄. After filtration and removal of the solvent, the crude product was purified by column chromatography (silica gel) using cyclohexane/ethyl acetate as eluent.

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