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Cascade Reaction of 6-Deoxy-6-Iodo-Hexopyranosides Promoted by Samarium Diiodide: A New Ring Contraction of Carbohydrate Derivatives†

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Supporting Information

General experimental procedure for the reaction of 6-deoxy-6-iodohexopyranosides with SmI_2. To a 0.1 M solution of SmI_2 in THF (20 mL, 2 mmol) was added HMPA (distilled from CaH_2 under Ar) (1,75 mL, 10 mmol) at room temperature. After stirring for 15 min, a solution of the 6-deoxy-6-iodohexopyranoside (0.33 mmol) in THF (6.5 mL) was added over 20 min. After stirring for 2 h at room temperature, the reaction mixture was diluted with EtOAc (25 mL) and washed with aqueous sat. $NaHCO_3$ (30 mL) and 10% aqueous $Na_2S_2O_3$ (20 mL), dried over anh. Na_2SO_4 and evaporated at reduced pressure. The crude residue was filtered through a small pad of silica gel to remove residual HMPA before ^1H NMR analysis to determine product ratios. Finally, the crude was purified by flash column chromatography in silica gel using hexane/EtOAc mixtures as eluent.

^{13}C NMR data for the cyclopentanes

Compound 8. ^{13}C NMR ($CDCl_3$) δ (DEPT 135° intensities) 170.3 (0), 169.8 (0), 112.3 (0), 83.4 (+), 82.8 (+), 81.4 (+), 81.0 (+), 43.8 (+), 26.9 (+), 24.7 (+), 20.85 (+), 20.80 (+), 15.5 (+).

Compound 9. ^{13}C NMR ($CDCl_3$) δ (DEPT 135° intensities) 170.5 (0), 170.4 (0), 170.1 (0), 112.3 (0), 82.6 (+), 81.8 (+), 81.4 (0), 80.8 (+), 79.6 (+), 44.5 (+), 42.0 (+), 27.0 (+), 26.5 (+), 26.0 (+), 24.7 (+), 22.4 (+), 20.9 (+).

Compound 10. ^{13}C NMR ($CDCl_3$) δ (DEPT 135° intensities) 170.1 (0), 169.2 (0), 111.5 (0), 84.7 (+), 82.3 (+), 80.6 (+), 40.3 (+), 26.0 (+), 24.0 (+), 20.85 (+), 20.81 (+), 8.32.

Compound 12. ^{13}C NMR (C_6D_6) δ (DEPT 135° intensities) 110.0 (0), 84.0 (+), 79.8 (+), 77.4 (+), 76.7 (+), 41.9 (+), 26.3 (+), 25.9 (+), 23.8 (+), 18.2 (0), 11.2 (+), -4.7 (+), -5.0 (+).

Comound 13. ^{13}C NMR (C_6D_6) δ (DEPT 135° intensities) 111.3 (0), 85.3 (+), 84.1 (+), 83.7 (+), 83.2 (+), 45.2 (+), 27.1 (+), 25.9 (+), 24.9 (+) 18.1 (0), 15.9 (+), -4.7 (+), -4.8 (+).

Compound 18. ^{13}C NMR (C_6D_6) δ (DEPT 135° intensities) 88.9 (+), 85.0 (+), 84.6 (+), 80.3 (+), 43.9 (+), 26.2 (+), 26.0 (+), 18.3 (0), 18.2 (0), 18.1 (0), 11.6 (+), -3.8 (+), -4.2 (+), -4.7 (+).

Comound 19. ^{13}C NMR (CD_3COCD_3) δ (DEPT 135° intensities) 87.2 (+), 84.7 (+), 79.9 (+), 78.6 (+), 46.8 (+), 26.3 (+), 26.2 (+), 26.1 (+), 18.8 (0), 18.5 (0), 18.4 (0), 16.9 (+), -3.9 (+), -3.8 (+), -4.1 (+), -4.2 (+), -4.3 (+).

Compound 21. ^{13}C NMR (C_6D_6) δ (DEPT 135° intensities) 82.4 (+), 82.0 (+), 80.3 (+), 79.8 (+), 48.3 (+), 26.4 (+), 26.1 (+), 26.0 (+), 16.8 (+), 18.6 (0), 18.4 (0), 18.1 (0), -4.1 (+), -4.2 (+), -4.3 (+), -4.4 (+), -4.5 (+).

Compound 22. ^{13}C NMR (C_6D_6) δ (DEPT 135° intensities) 83.2 (+), 80.2 (+), 78.6 (+), 78.4 (+), 38.1 (+), 26.4 (+), 26.0 (+), 25.9 (+), 18.5 (0), 18.3 (0), 18.1 (0), 9.3 (+), -4.2 (+), -4.5 (+), -4.9 (+).

Compound 24. ^{13}C NMR (CD_3COCD_3) δ (DEPT 135° intensities) 84.4 (+), 84.0 (+), 80.0 (+), 78.8 (+), 45.9 (+), 26.3 (+), 26.2 (+), 26.1 (+), 18.6 (0), 18.55 (0), 18.3 (0), 16.8 (+), -4.0 (+), -4.1 (+), -4.25 (+), -4.3 (+), -4.4 (+), -4.6 (+).

Compound 25. ^{13}C NMR (C_6D_6) δ (DEPT 135° intensities) 83.2 (+), 80.2 (+), 78.6 (+), 78.4 (+), 38.1 (+), 26.4 (+), 26.0 (+), 25.9 (+), 18.6 (0), 18.3 (0), 18.1 (0), 9.3 (+), -4.2 (+), -4.5 (+), -4.9 (+).

Compound 27. ^{13}C NMR ($CDCl_3$) δ (DEPT 135° intensities) 170.1 (0), 169.5 (0), 110.6 (0), 81.4 (+), 78.4 (+), 75.7 (+), 74.9 (+), 38.5 (+), 25.9 (+), 23.6 (+), 20.6 (+), 20.5 (+), 10.5 (+).

Compound 28-d_1. ^{13}C NMR ($CDCl_3$) δ (DEPT 135° intensities) 170.3 (0), 169.7 (0), 112.7 (0), 83.8 (+), 82.3 (+), 78.0 (+), 76.4 (0), 41.0 (+), 26.8 (+), 24.4 (+), 20.6 (+), 20.5 (+), 12.1 (-, t, J = 9.4 Hz).

Table 1. ^{1}H NMR chemical shifts (δ) and coupling constants (J, Hz) for the cyclopentane products.

	8[a]	**9**[a]	**10**[a]	**12**[a]	**13**[b]	**18**[c]	**19**[c]	**21**[c]	**22**[c]	**24**[a]	**25**[b]	**27**[a]	**28-d_1**[a]
H-1	4.88	4.96	5.09	3.69	3.39	3.72	~3.57	3.67	3.95	3.72	3.34	4.93	5.38
H-2	5.14	5.15	5.02	3.92	4.10	3.76	~3.78	4.04	4.15	3.94	3.82	5.20	~5.16
H-3	4.49	4.46	4.46	4.24	4.24	3.81	~3.78	3.77	3.80	3.82	3.75	4.40	4.58
H-4	4.25	4.36	4.63	4.46	3.92	3.70	3.52	3.54	3.87	4.10	3.69	4.54	4.36
H-5	2.26	2.35	2.38		2.07	2.02	~1.98	1.64	2.46	1.81	2.05	2.25	2.34
CH_2R	1.10	1.79 1.98	1.10	1.11	0.98	1.03	1.12	1.18	0.90	1.06	1.09	1.07	~1.06
OH	-	-	-	1.85	1.81	3.85	3.08	3.94	3.32	2.50	3.67	-	-
$J_{1,2}$	5.7	6.7	1.0	4.5	6.0	1.5	~3	7.0	5.6	5.8	2.7	4.4	4.6
$J_{1,3}$	0	-	0	0	0	1.6	0	0	0	0	1.1	0	-
$J_{1,5}$	7.3	8.7	5.3	11.0	7.2	4.0	~9	5.7	8.8	4.9	6.3	11.5	4.7
$J_{1,OH}$	-	-	-	11.2	6.8	7.0	8.1	5.6	6.5	~7.2	6.6	-	-
$J_{2,3}$	2.9	4.0	1.3	~0	3.3	1.6	-	3.6	3.8	4.5	2.5	~0	3.8
$J_{2,4}$	0	-	0	0	0	0.7	1.3	0	0	0	0	0	-
$J_{3,4}$	6.8	7.2	5.9	6.1	6.9	4.9	1.4	2.2	2.2	3.4	3.7	6.1	8.1
$J_{3,5}$	0	-	0	0	0	0	0	1.3	0	0	0	0	0
$J_{4,5}$	4.7	4.7	5.5	5.3	4.6	~9.3	5.9	2.6	5.3	7.3	8.3	5.3	6.0
$J_{5,CHR}$	7.3	3.7, 0, -14.6	7.2	6.9	7.2	6.9	7.0	7.4	7.3	7.3	7.0	6.9	n.d.

[a] In $CDCl_3$.

[b] In C_6D_6.

[c] In CD_3COCD_3.

Table 2. Significant NOE effects for the cyclopentane compounds (s: strong; m: medium; w: weak).

	8[a]	**9**[a]	**10**[a]	**12**[a]	**13**[b]	**18**[c]	**21**[c]	**22**[c]	**24**[a]	**25**[c]	**28**[a]
H-1 / H-2		w		s	w		w	w	s		s
H-1 / H-3		w			w					w	
H-1 / H-4	m	w								m	
H-1 / H-5		w	s	w		s	w	s	w	w	s
H-2 / H-5	m	m			m		w				m
H-3 / H-5				w		m			m		
H-4 / H-5		w	s	s				s	s		w
H-1 / Me	s			s	s	w	s		s	s	
H-2 / Me						w					
H-3 / Me	w										
H-4 / Me	s			w	s	s	s			s	

[a] In $CDCl_3$
[b] In C_6D_6
[c] In CD_3COCD_3