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The Synthesis of Iodoglyoxalic Esters. Cleavage of Tetrahydrofuran and 1,2-Dimethoxyethane[1)]

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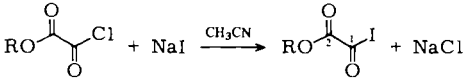
Die Synthese von Iodglyoxylsäureestern. Spaltung von Tetrahydrofuran und 1,2-Dimethoxyethan[1)]

Eine Serie von Iodglyoxylaten **2a – i** wird aus Chlorglyoxylaten **1a – i** und Natriumiodid in Acetonitril dargestellt und durch Tieftemperaturextraktion mit Pentan isoliert. Iodglyoxylsäureester eignen sich zur acylierenden Spaltung von Ethern, z. B. Tetrahydrofuran und 1,2-Dimethoxyethan.

Iodoglyoxalic esters have not yet been described, although chloroglyoxalic esters[2)] (**1**) are well known[3)]. We report the preparation, isolation, and acylative cleavage reactions of representative iodoglyoxalates (**2a – i**), which we obtained by the reaction of **1** with sodium iodide in acetonitrile and extraction into pentane, using our low-temperature reactor-extractor[4)]. All chloroglyoxalates **1a – i** reacted smoothly with sodium iodide at 25 °C or below, irrespective of the type of alkyl group R.



1 **2**

Having observed earlier that the relatively polar acetyl iodide and also malonyl diiodide can not be extracted from acetonitrile into pentane[4)], we now found that all iodoglyoxalic esters could be extracted with pentane, even the simple methyl iodoglyoxalate (**2a**), which must be the least lipophilic compound in the series of iodoglyoxalates **2a – i**. In fact, extraction times of 3 – 5 hours sufficed to isolate **2a – i** in high yields (Table 1).

The ^{1}H NMR spectra of chloroglyoxalates **1** and corresponding iodoglyoxalates **2** showed little difference, i.e. the Cl/I exchange has little effect on the signal of protons which are necessarily remote from the halocarbonyl group. In contrast, the ^{13}C NMR spectra were more informative by virtue of two additional signals, i.e. those of the carbonyl carbons C-1 and C-2 (Table 2).

Within the series of iodoglyoxalates the signal of the terminal C-1 carbon changes over a narrower range (δ_1 = 150.6 to 154.8) than that of C-2 (δ_2 = 145.4 to 151.2), C-2 being closer to the site of structural change. The signals of the corresponding two carbonyl carbons of the chloroglyoxalates **1a – i** behave similarly. The ^{13}C NMR signal of the iodocarbonyl carbon in **2** is shifted upfield from that of the chlorocarbonyl carbon in **1** ($\Delta\delta_1$ negative, heavy atom effect of iodine), in agreement with earlier observations on acyl iodides[4,5)].

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Table 1. Iodoglyoxalates (**2a–i**) from Chloroglyoxalates (**1a–i**)

1(X=Cl), **2**(X=I)	b.p. of **1** [°C]/Torr	Reaction Time [h]	Extraction Time [h]	Yield[a] [%]	Molecular Formula[b]
a $CH_3O\overset{2}{C}O\overset{1}{C}OX$	120	0.5	5	50	$C_3H_3IO_3$ (214.0)
b $C_2H_5OCOCOX$	135	0.5	4	53	$C_4H_5IO_3$ (228.0)
c $CH_3[CH_2]_7OCOCOX$	106/9	0.5	3	85	$C_{10}H_{17}IO_3$ (312.3)
d 	122/34	0.5	4	97	$C_8H_{11}IO_3$ (282.2)
e $i\text{-}C_3H_7OCOCOX$	55/33	0.5	4	81	$C_5H_7IO_3$ (242.1)
f 	110/1[c]	0.5	3	90	$C_{12}H_{15}IO_3$ (334.2)
g $t\text{-}C_4H_9OCOCOX$	52/22	0.5	3	85	$C_6H_9IO_3$ (256.2)
h 	89/6	0.5	4	88	$C_8H_5IO_3$ (276.1)
i 	125/1	0.5	4	75	$C_8H_2Cl_3IO_3$ (379.5)

[a] Yields of isolated product obtained by standard procedure. The yields have not been optimized. – [b] Sufficiently correct microanalyses cannot be obtained because of instability of the products **2**. Any decomposition products in amounts of 5% or more would have been detected in the ^{13}C NMR spectra. – [c] Sublimation.

Table 2. ^{13}C NMR ($CDCl_3/TMS_{int}$) Data of Iodoglyoxalates (**2a–i**) and Chloroglyoxalates (**1a–i**), δ[ppm]

Compound	δ_1	δ_2	$\Delta\delta_1$[a]	$\Delta\delta_2$[a]	Other signals
1a	161.1	156.4			55.2
2a	154.8	149.8	−6.3	−6.6	55.3
1b	161.2	155.9			65.3 13.9
2b	154.3	150.4	−6.9	−5.5	65.4 13.8
1c	161.0	156.0			69.1 31.9–14.1 (6 signals)
2c	154.5	150.5	−6.5	−5.5	69.3 31.7–14.1 (6 signals)
1d	161.2	155.2			78.5 31.2 25.2 23.4
2d	153.5	150.5	−7.7	−4.7	78.7 30.9 25.1 23.2
1e	161.3	155.4			74.1 21.4
2e	153.8	150.7	−7.5	−4.7	74.4 21.4
1f	160.9	154.8			82.8 36.9–26.7 (6 signals)
2f	153.4	150.2	−7.5	−4.6	83.4 37.1–26.7 (6 signals)
1g	161.4	154.7			87.7 27.1
2g	152.9	151.2	−8.5	−3.5	87.8 27.4
1h	160.9	154.0			130.0 127.3 120.6
2h	152.7	150.0	−8.2	−4.0	129.9 127.3 120.4
1i	159.1	152.0			141.7 133.8 129.0
2i	150.6	145.4	−8.5	−6.6	141.3 133.6 128.9

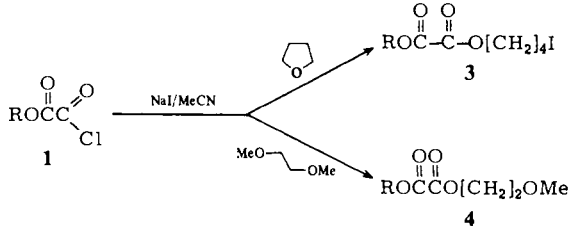
[a] Chemical shift difference for C-1 and C-2, respectively, on going from iodoglyoxalate to chloroglyoxalate.

Table 3. IR Data (CCl_4) of **1a–i** and **2a–i**, ν[cm^{-1}]

1a	1795s,	1770vs,	1440m,	1265s,	1020s		
2a	1784vs,	1760s,	1435m,	1264vs,	995s		
1b	1795s,	1762vs,	1253s,	1022s			
2b	1780vs,	1754s,	1237vs,	1012s			
1c	1785s,	1770vs,	1468m,	1264vs,	1218s,	987m	
2c	1782vs,	1757s,	1468m,	1235s,	1217vs,	950m	
1d	1787s,	1755vs,	1450m,	1260w,	988s		
2d	1784vs,	1750s,	1450m,	1240w,	958m		
1e	1790s,	1788vs,	1277s,	987m			
2e	1785vs,	1752s,	1248s,	952m			
1f	1788s,	1754vs,	1454w,	1265s,	1218vs,	990s	
2f	1785vs,	1755s,	1453w,	1245vs,	1218s,	965s	
1g	1800s,	1776s,	1755vs,	1372m,	1280s,	1155s,	973s
2g	1787vs,	1752s,	1373m,	1255s,	1152s,	940s	
1h	1785vs,	1770s,	1490s,	1236vs,	962s		
2h	1775s,	1744s,	1490s,	1200vs			
1i	1791vs,	1772m,	1570s,	1458s,	1234s,	950vs	
2i	1787vs,		1570m,	1445s,	1188v,	918vs	

In the IR a shift of selected bands in **2a–i** to lower wave numbers could be discerned (Table 3).

Iodoglyoxalic esters cleave tetrahydrofuran and 1,2-dimethoxyethane with formation of functionalized oxalic esters **3** and **4**, respectively, at room temperature (Table 4).



Cleavage of tetrahydrofuran is especially easy[6]. In summary, the acylative cleavage of basic and sterically accessible ethers with iodocarbonyl compounds gives useful synthetic intermediates. The reaction can also be used for the deprotection of alcohols.

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Experimental Part

Iodoglyoxalic Esters **2**, *General Procedure* (Table 1): Dry, finely powdered sodium iodide (7.5 g, 50 mmol) is placed into the reaction vessel of the reactor-extractor[4]. The apparatus is flame-dried *in vacuo* and flushed with nitrogen. Absol. acetonitrile (70 ml), redistilled from P_4O_{10}, is introduced to dissolve the sodium iodide and chloroglyoxalic ester[7] (**1**) (30 mmol) is added by injection. The resulting solution is stirred at room temperature, turning yellow with precipitation of finely divided sodium chloride. After 30 min the reaction mixture is extracted with absol. pentane (redistilled from $LiAlH_4$) for 3–5 h under slightly reduced pressure (150–200 Torr), while the mother liquor is kept at −25 °C and the receiving vessel at 30 °C[4].

Table 4. Mixed Oxalic Esters **3** and **4** from Chloroglyoxalic Esters (**1**), Sodium Iodide, and THF or DME, respectively

1	Ether cleaved	Reaction Time [h]		Product	Yield [%]	b.p./Torr [°C], Kugelrohr	Molecular Formula	IR ν[cm^{-1}] (CCl_4)
1a	THF	22	**3a**	$CH_3OCOCO_2[CH_2]_4I$	80	80/< 1	$C_7H_{11}IO_4$ [a] (285.9702)	1775, 1750
1b	THF	20	**3b**	$C_2H_5OCOCO_2[CH_2]_4I$	85	100/< 1	$C_8H_{13}IO_4$ [b] (299.9859)	1770, 1745
1c	THF	20	**3c**	n-$C_8H_{17}OCOCO_2[CH_2]_4I$	80	120/< 1	$C_{14}H_{25}IO_4$ [c] (384.0798)	1770, 1745
1a	DME	22	**4a**	$CH_3OCOCO_2[CH_2]_2OCH_3$	40	–	$C_6H_{10}O_5$ [d] (162.1)	1775, 1750
1b	DME	22	**4b**	$C_2H_5OCOCO_2[CH_2]_2OCH_3$	40	85/0.05	$C_7H_{12}O_5$ [d] (176.2)	1770, 1745
1c	DME	28	**4c**	n-$C_8H_{17}OCOCO_2[CH_2]_2OCH_3$	30	150/0.05	$C_{13}H_{24}O_5$ [d] (260.3)	1775, 1750

[a] MS: m/e = 285.9702 (M^+). – [b] MS: m/e = 299.9859 (M^+). – [c] MS: m/e = 384.0799 (M^+). – [d] Compounds pure by gaschromatographic standards.

Table 5. ^{1}H NMR Data of Functionalized Oxalic Esters **3** and **4**

	δ[ppm] ($CDCl_3$, TMS_{int})
3a	1.70 – 2.05 (*m*, 4H); 3.11 – 3.33 (*m*, 2H); 3.90 (s, 3H); 4.30 – 4.41 (m, 2H)
3b	1.38 (t, 3H); 1.70 – 2.16 (m, 4H); 3.10 – 3.22 (m, 2H); 4.31 (t, 2H); 4.36 (q, 2H)
3c	0.80 (br t, 3H); 1.30 (br, 10H); 1.56 – 1.80 (m, 2H); 1.80 – 1.95 (m, 4H); 3.30 – 3.11 (m, 2H); 4.18 – 4.44 (m, 4H)
4a	3.40 (s, 3H); 3.87 – 3.60 (m, 2H); 3.90 (s, 3H); 4.35 – 4.50 (m, 2H)
4b	1.50 (t, 3H); 3.50 (s, 3H); 3.73 – 3.90 (m, 2H); 4.33 – 4.60 (m, 2H); 4.50 (m, 2H)
4c	0.87 (br t, 3H); 1.30 (*br. s, 10H*); 1.55 – 1.90 (*m, 2H*); 3.40 (*s*, 3H); 3.60 – 3.74 (m, 2H); 4.28 (t, 2H); 4.35 – 4.50 (m, 2H)

After evaporation of the pentane the resulting iodoglyoxalic ester is at least > 95% pure by ^{13}C NMR.

Cleavage of Ethers with Formation of **3, 4** *(Table 4):* Dried sodium iodide (3.0 g, 20 mmol) was dissolved in absol. acetonitrile (15 ml) under nitrogen. Chloroglyoxalate (**1**) (10 mmol) in acetonitrile (1 ml) was injected at room temperature with precipitation of NaCl. After 30 min an excess of ether (ca. 3 ml of tetrahydrofuran) was added. The reaction mixture became warm and was stirred for 2 h. The mixture was worked up by adding water (40 ml) and extracting with ether (3 × 30 ml). The organic phase was washed with 5% solution (20 ml) of aqueous $Na_2S_2O_3$ until it was free from iodine and dried (Na_2SO_4). After removal of the solvent the residue was distilled at reduced pressure over copper powder in a Kugelrohr apparatus.

Cleavage of 1,2-dimethoxyethane was carried out in the temperature range 0 – 25 °C, and the reaction mixture was kept overnight at room temperature before being worked up.

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