The Synthesis of Acyl Iodides

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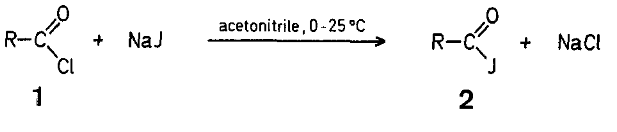
Acyl iodides[1] have hitherto attracted little attention although their synthesis had already been attempted in the beginnings of organic chemistry. In 1832, Liebig and Wöhler reported that treatment of benzoyl chloride with potassium iodide produces benzoyl iodide which they described as a crystalline compound[2] (doubted by Thiele[3]). Acetyl iodide was later prepared by heating acetic anhydride with red phosphorus and iodine[4], and acetyl as well as benzoyl iodide were prepared by reaction of the corresponding chlorides with gaseous hydrogen iodide and evaporation of the resultant hydrogen chloride[5]. A number of halogenated acyl iodides[6] and substituted benzoyl iodides[7] were synthesized by this latter method. New methods for preparing acyl halides including acyl iodides have recently been reported[8].

We report here that a large number of alkanoyl, alkenoyl, and aroyl iodides (**2**) can be prepared in good yields from the corresponding acyl chlorides (**1**) and sodium iodide in acetonitrile, using an improved version of our earlier described low-temperature reactor-extractor, which had allowed us to obtain highly reactive heterocyclic α-aminoacetals[9,10]. Isolation of the product acyl iodides involves extraction of the acetonitrile mother liquor with pentane or 2-methylbutane.



The reaction of acyl chlorides (**1**) with sodium iodide proceeds readily and seems to be little affected by steric factors. For example, 2,2-dimethylpropanoyl iodide (**2i**) is obtained in 80% yield under the usual conditions; even the sterically hindered 2,4,6-trimethylbenzoyl (**1z$_3$**) and 2,3,5,6-tetramethylbenzoyl chlorides (**1z$_4$**) are converted into the corresponding iodides (**2z$_3$**, **2z$_4$**) in high yields.

Octanoyl iodide (**2d**) and similar acyl iodides are so lipophilic that they can be isolated by a single extraction with pentane in a separatory funnel. On the other hand, the very polar acetyl iodide (**2a**) forms an azeotrope with acetonitrile and can therefore not be extracted from this solvent. The homologous propanoyl iodide (**2c**) is isolated in 53% yield after an extraction time of 20 h whereas trichloroacetyl iodide (**2n**) is isolated in 85% yield after an extraction time of only 5 h.

3-Chloropropanoyl chloride (**1k**) is attacked by iodide ion preferentially (>90%) at the chlorocarbonyl C-atom (sp^2) than at the saturated C-3 atom (sp^3). The homologous chloride **1m** gives **2m** exclusively. Even 3-bromopropanoyl chloride (**1l**) which possesses the potentially better bromide leaving group reacts at 0 °C to form mainly **2l**. These examples show the high selectivity of our method (Table 2).

Using a larger capacity reactor-extractor, the method can be applied to larger-scale preparations without decrease in yield (as found in the preparations of **2r** and **2s**).

Simple acyl iodides (**2**) are generally heavy liquids. Adamantane-1-carbonyl iodide (**2j**) forms slightly yellowish crystals. Similarly, phenoxyacetyl iodide (**2p**) is a solid, whilst the corresponding chloride (**1p**) is a liquid at room temperature. All acyl iodides (**2**) hitherto obtained are readily soluble in dichloromethane, but less soluble in pentane. We therefore store the acyl iodides in dichloromethane as solvent. Most acyl iodides react instantaneously with water.

In the I.R. spectrum, the carbonyl band of the acyl iodides, as compared to that of the chlorides, is changed only slightly, being broadened or shifted at most by 5 cm^{-1} to lower wave numbers. In the finger-print region, a shift of a few selected bands by 20–30 cm^{-1} to lower wave numbers was detected (Perkin Elmer 580, CCl_4 or NaCl).

For proving the structure of the acyl iodides (**2**), ^{13}C-N.M.R. spectrometry is especially helpful, because all signals are generally well resolved and can be compared with those of corresponding acyl chlorides (Table 3). In all acyl iodides (**2**) investigated, the signal of C-1 appears upfield (Table 3, $\Delta\delta_1$ negative) from the signal of C-1 in the corresponding chloride (**1**) (heavy-atom effect of iodine). Typically, for a primary alkyl group R in RCOJ, $\Delta\delta_1 = -11$ to -13; for a secondary alkyl, $\Delta\delta_1 = -8$ to -11 and for a tertiary alkyl group, $\Delta\delta_1 = -2.5$ to -5. On the other hand, the signal of C-2 of **2** is shifted downfield from the corresponding signal of **1**. The Cl/J exchange has only little effect on the signals of C-atoms more remote from the halocarbonyl group (see, for example, the signals of the CH_3 groups of the propanoyl halides **1c** and **2c** in Table 3).

The ^{13}C-N.M.R. spectra may also be used for a purity determination of products **2**. In the simple proton-decoupled spectra of compounds **2**, any decomposition products present in amounts of 5% or more would be detected by additional peaks. The absence of such peaks is in accord with the high-resolution ^{1}H-N.M.R. spectra of freshly prepared samples of compounds **2**; integration of these spectra shows that compounds **2** are at least 95% pure.

In the ^{1}H-N.M.R. spectra, the signal of the 2-H atom of alkanoyl iodides tends to be downfield from the corresponding signal of the chlorides.

As regards the 2-alkenoyl (**2q–t**) and benzoyl (**2u–z$_4$**) iodides, the signal of the iodocarbonyl C-atom is also found upfield from the corresponding signal of the chlorides **1** (heavy-atom effect of iodine)[13], and the signal of the C-atom linked to the iodocarbonyl group (C-2 of alkenoyl iodides or C-1 of benzoyl iodides) appears downfield from the corresponding signal of **1**, thus suggesting that the iodocarbonyl group is the better σ-acceptor. It is difficult to draw conclusions about the π-acceptor qualities of the iodocarbonyl group, because the conformation of the various molecules to be compared is not known. The two most simple olefinic acyl iodides **2q** and **2t** offer even less steric hindrance to π-overlap than the simplest aromatic acyl iodide, benzoyl iodide (**2u**). The signals of C-3 of compounds **2q** and **2t** appear downfield from the corresponding signals of **1q** and **1t**, suggesting that the iodocarbonyl group is a better π-acceptor than the chlorocarbonyl group. With increasing substitution of the C=C double bond, the halocarbonyl moieties are expected to be twisted out of the plane of the neighbouring π-system, iodocarbonyl more so than chlorocarbonyl, and a discussion of chemical shifts for the olefinic acyl iodides becomes more problematic[14]. The crowded aromatic acyl iodide, 2,4,6-trimethylbenzoyl iodide (**2z$_3$**), must have its iodocarbonyl group rotated out of the plane of the aromatic ring. Consistently, $\Delta\delta_2$ and $\Delta\delta_6$ are now negative by a comparative large amount, i.e. -7.0 (Table 5), whereas $\Delta\delta_1 = 7.3$. The ^{19}F-N.M.R. shift of 4-fluorobenzoyl iodide (**2x**) appears 0.5 ppm upfield from the signal of the chloride **1x**, suggesting that iodocarbonyl, when attached to an aromatic nucleus, is a slightly poorer or comparable π-acceptor.

In general, simple benzoyl iodides appear to be more stable than aliphatic acyl iodides, undoubtedly because of stabilization by π-overlap in the ground state. For comparison, it is well-known that acetyl chloride reacts almost explosively with cold water, whilst benzoyl chloride (**1u**) reacts very slowly. However, 2,4,6-trimethylbenzoyl iodide (**2z$_3$**) is comparable in reactivity to aliphatic acyl iodides[15]; it also fumes

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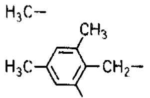
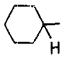
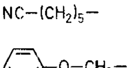
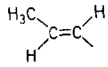
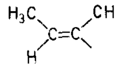
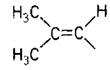
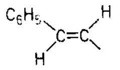
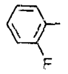
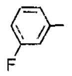
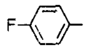
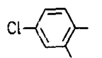
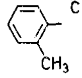
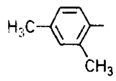
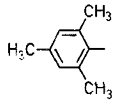
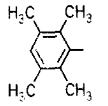
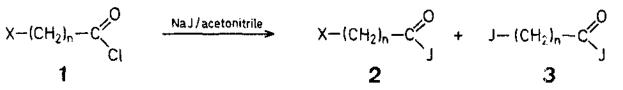
Table 1. Acyl Iodides (**2**) from Acyl Chlorides (**1**)

1,**2**	R	m.p. [°C] or b.p. [°C]/torr of **1**	Reaction time [h]	Extraction time [h]	Yield[a] [%]	Molecular formula[b] or b.p./torr [°C] reported	
a	H_3C-	[c]	—	—	[c]	C_2H_3JO	(169.9)
b		b.p. 130°/10	0.75	5.5	62	$C_{11}H_{13}JO$	(288.1)
c	C_2H_5-	b.p. 77–79°	1	20	53	b.p. 52–53°/50[8]	
d	$n\text{-}C_7H_{15}-$	b.p. 89°/20	0.5	18	90 (38)[d]	$C_8H_{15}JO$	(254.1)
e	$i\text{-}C_3H_7-$	b.p. 92°	0.75	5	74	C_4H_7JO	(198.0)
f			0.5	6	83	C_4H_5JO	(196.0)
g			0.5	5	92	C_5H_7JO	(210.0)
h		b.p. 75–77°/15	0.75	5	75	$C_7H_{11}JO$	(238.1)
i	$t\text{-}C_4H_9$	b.p. 107°	1	7.5	80 (48)[d]	C_5H_9JO	(212.0)
j		m.p. 49–51°	0.75	5	93	$C_{11}H_{15}JO$	(290.1)
k	$Cl-CH_2-CH_2-$	b.p. 143°	0.5	18	57	C_3H_4ClJO	(220.4)
l	$Br-CH_2-CH_2-$	b.p. 173°	1	19	83 (47)[d]	C_3H_4BrJO	(262.9)
m	$Cl-CH_2-CH_2-CH_2-$	b.p. 55–57°/17	0.5	15	63	C_4H_6ClJO	(232.4)
n	Cl_3C-		0.1	5	85	C_2Cl_3JO	(273.3)
o	$NC-(CH_2)_5-$	b.p. 135°/1	0.75	20	24	$C_7H_{10}JNO$	(251.1)
p		b.p. 111°/13	0.5	6	75	$C_8H_7JO_2$	(262.0)
q	 (*E*)	b.p. 120°[e]	0.5	17 (7)	91 (66)[d]	C_4H_5JO	(196.0)
r	 (*E*)	b.p. 34°/35	0.5	6	88	b.p. 133–135°/24[8]	
s		b.p. 145°	0.5	6	88	C_5H_7JO	(210.0)
t	 (*E*)	m.p. 35–37°	1 (0.5)	8 (6)	97 (30)[d]	C_9H_7JO	(258.1)
u			1 (0.5)	6 (7)	90 (62)[d]	C_7H_5JO	(232.0)
v		b.p. 85°/20	1	8	95	C_7H_4FJO	(250.0)
w		b.p. 90°/15	1	8	95	C_7H_4FJO	(250.0)
x		b.p. 82°/20	1	8	92	C_7H_4FJO	(250.0)
y		m.p. 18°	2	6	88	$C_7H_3Cl_2JO$	(300.9)
z₁			1	8	93	C_8H_7JO	(246.0)
z₂		b.p. 113°/15	1	8	96	C_9H_9JO	(260.1)
z₃		b.p. 116°/18	0.5	6	95 (80)[d]	$C_{10}H_{11}JO$	(274.1)
z₄		m.p. 61°	1	20	92	$C_{11}H_{13}JO$	(288.1)

[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.
[c] Isolation by standard procedure not possible.
[d] Yields obtained in initial experiments.
[e] Acyl chloride **1q** has to be separated from thionyl chloride by distillation over a 20 cm Vigreux column.

Table 2. Selectivity of Halide Displacement in ω-Haloalkanoyl Chlorides (**1k, l, m**)



1		Ratio **2** : **3**
k	X=Cl, n=2	90 : 10
l	X=Br, n=2	80 : 20[a]
m	X=Cl, n=3	100 : 0

[a] Reaction at 0 °C.

Table 3. ^{13}C-N.M.R. (CDCl$_3$/TMS$_{int}$) *Data of Alkanoyl Chlorides* (**1a–p**) *and* Alkanoyl Iodides (**2a–p**), δ [ppm] (cf. Ref.[13])

Compound	δ_{C-1}	δ_{C-2}	$\Delta\delta_1$[a]	$\Delta\delta_2$[a]	Other signals
1a	169.5	24.2			
2a[b]	159.8	33.9	− 9.7	9.7	
1b	171.8	47.3			137.9; 137.3; 129.4; 126.7 (C_{arom}); 21.0; 20.1 (CH_3)
2b	160.3	60.3	−11.5	13.0	138.1; 136.9; 129.3; 127.8 (C_{arom}); 21.0; 20.5 (CH_3)
1c	174.7	41.0			9.6 (CH_3)
2c	162.9	54.1	−11.8	13.1	10.3 (CH_3)
1d	173.4	47.3			31.8; 29.0; 28.7; 25.4; 22.7; 14.1
2d	162.2	60.3	−11.2	13.0	31.5; 28.7; 27.9; 25.6; 23.5; 14.0
1e	177.9	46.5			19.0 (CH_3)
2e	169.7	56.5	− 8.2	10.0	18.4 (CH_3)
1f	175.2	23.9			12.4
2f	164.2	33.2	−11.0	9.3	13.1
1g	175.6	49.3			26.3; 17.5
2g	166.5	60.4	− 9.1	11.1	27.0; 15.8
1h	176.8	55.1			29.4; 25.1; 25.6
2h	168.8	65.8	− 8.3	10.7	29.0; 24.6; 25.5
1i	180.3	49.4			27.2 (CH_3)
2i	175.3	54.6	− 5.0	5.2	26.6 (CH_3)
1j	179.7	51.2			39.2; 28.1; 36.3
2j	177.2	56.7	− 2.5	5.6	39.5; 28.0; 36.2
1k	171.2	49.3			38.1
2k	157.8	61.0	−13.4	11.7	37.9
1l	171.3	49.2			24.2
2l	158.3	62.4	−12.0	13.2	24.4
1m	173.2	44.1			43.1; 27.8
2m	160.6	57.3	−12.9	13.2	42.4; 28.1
1n	163.3	94.2			
2n	147.2	99.8	−16.1	5.6	
1o	173.5	46.6			119.6 (C≡N); 27.4; 24.9; 24.2; 16.8
2o	161.9	59.2	−11.6	12.9	119.1 (C≡N); 26.5; 24.8; 24.5; 16.6
1p	176.3	71.4			157.1; 129.9; 122.8; 115.0
2p	160.4	82.1	−15.9	10.7	156.5; 129.7; 122.7; 114.8

[a] Chemical shift difference for C-1 etc., on going from acyl iodide to acyl chloride. With increasing distance of C-n from the halocarbonyl carbon C-1, $\Delta\delta_n$ ($n \geq 3$) decreases.

[b] Acetyl iodide (**2a**) was prepared by the reaction of sodium acetate with red phosphorus and iodine; see Ref.[4].

when exposed to air. Cyclic voltammetry has shown that **2u** and **2z$_3$** are oxidized readily (0.47 V and 0.35 V, respectively), comparable to enamines. In contrast, reduction requires more forcing conditions, i.e. −1.77 V for **2u** and −1.75 to −1.90 for **2z$_3$**[16]. Finally, 4-fluorobenzoyl iodide (**2x**) is a colorless crystalline solid which could be kept under nitrogen for several months without decomposition.

Our low-temperature reactor-extractor as well as the experimental procedure are more widely applicable and may, for instance, be used (with modifications) for the preparation of other reactive iodine-containing compounds and for handling and isolation of sensitive compounds in general[9, 17].

The acyl chlorides **1** used in the conversion should be of high purity. We have prepared commercially not available acyl chlorides by the *following three methods:*

- in the standard procedure, the carboxylic acid is refluxed with thionyl chloride (1.5 equiv) and the product **1** is isolated by distillation over a Vigreux column;
- low-boiling acyl chlorides (e.g., **1c** and **1i**) are obtained by the procedure of Ref.[11] using 2 mol equivalents of benzoyl chloride (which is a comparatively involatile chlorinating agent: b.p. 198 °C). [In an attempt to prepare **1i** using thionyl chloride, the product **1i** (b.p. 104 °C) was found to contain thionyl chloride (b.p. 75–76 °C) which was decomposed under the conditions of the iodination];
- certain sensitive acyl chlorides such as 3,5-hexadienoyl chloride[12] are prepared by treatment of the carboxylic acid with oxalyl chloride (b.p. 62 °C, 1.2 equiv) in dichloromethane in the presence of potassium carbonate at room temperature and the products are isolated by Kugelrohr distillation.

Acyl Iodides (2) from Acyl Chlorides (1); General Procedure:

Apparatus:

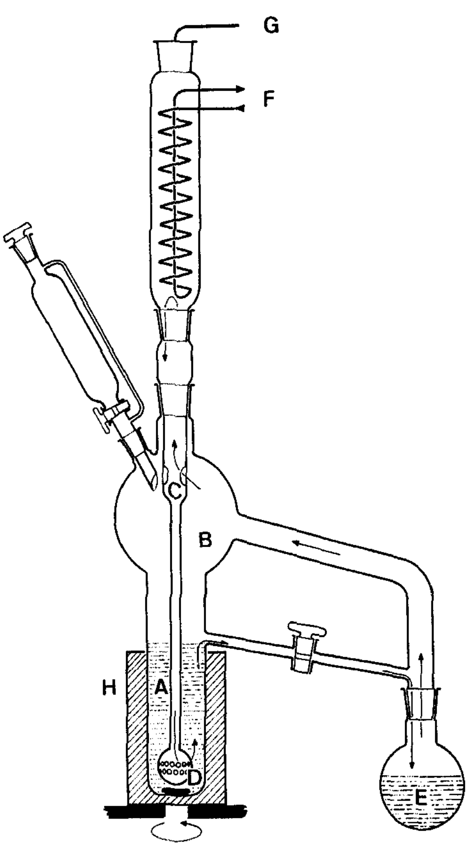


Figure. Low-Temperature Reactor-Extractor (cf. Ref.[9]) (drawn in correct scale)

A Reaction vessel (~220 ml capacity up to overflow). During extraction this vessel is cooled externally with the coolant from the condenser.
B Extraction tube.
C Pentane inlet.
D Pentane outlet. The perforated bulb and a magnetic stirrer ensure an efficient distribution of pentane in the acetonitrile phase.
E Extraction flask.
F Inlet for coolant (−25 °C).
G Connection to vacuum pump (~150–200 torr).
H Cooling bath.

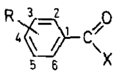
Reaction: Dry, finely powdered sodium iodide (15 g, 0.10 mol) is placed into the reaction vessel A of the reactor-extractor. The apparatus is assembled and flame-dried in a stream of nitrogen. All further *manipulations are carried out in a countercurrent of nitrogen.* Absolute acetonitrile (100 ml) redistilled from phosphorus pentoxide is

Table 4. ^{13}C-N.M.R. (CDCl$_3$/TMS$_{int}$) Data of 2-Alkenoyl Chlorides (**1q–t**) and 2-Alkenoyl Iodides (**2q–t**), δ [ppm].

Compound	δ_{C-1}	δ_{C-2}	δ_{C-3}	$\Delta\delta_1$[a]	$\Delta\delta_2$[a]	$\Delta\delta_3$[a]	Other signals
1q	165.3	127.8	152.8				18.2
2q	155.2	133.1	155.1	−10.1	5.3	2.3	18.2
1r	168.8	133.9	147.9				15.4; 13.2
2r	161.3	136.2	154.0	− 7.5	2.3	6.1	15.2; 12.3
1s	163.5	122.6	164.4				27.3; 21.6
2s	160.6	133.6	152.1	− 2.9	11.0	−12.3	26.6; 22.8
1t	167.2	122.2	150.6				133.0; 132.1; 130.3; 130.2 (C$_{arom}$)
2t	155.0	128.4	151.6	−12.2	6.2	1.0	132.3; 132.2; 129.4; 129.3 (C$_{arom}$)

[a] Chemical shift difference for C-1, C-2 etc., on going from acyl iodide to acyl chloride.

Table 5. ^{13}C-N.M.R. (CDCl$_3$/TMS$_{int}$) Data of Benzoyl Chlorides (**1u–z$_4$**) and Benzoyl Iodides (**2u–z$_4$**), δ [ppm]

Compound	C=O	C-Atoms of Phenyl Ring 						Other signals
		C-1	C-2	C-3	C-4	C-5	C-6	
1u	168.0	133.3	131.3	129.0	135.4	129.0	131.3	
2u	159.5	136.3	131.9	128.6	135.4	128.6	131.9	
	− 8.5	3.0	0.6	−0.4	0.0	−0.4	0.6	
1v	163.0	121.9	161.9	117.3	137.2	134.2	124.8	
2v	151.5	124.6	157.8	116.6	136.8	137.2	124.8	
	−11.5	2.7	−4.1	−0.7	−0.4	3.0	0	
1w[a]	167.2	135.5	118.6	162.1	122.7	130.9	127.3	
2w[a]	157.4	138.8	118.5	162.1	122.5	130.2	127.9	
	− 9.8	3.3	−0.1	0	−0.2	−0.7	0.6	
1x[a]	166.9	129.7	134.4	116.0	167.4	116.0	134.4	
2x[a]	157.4	133.2	134.9	116.0	167.5	116.0	134.9	
	− 9.5	3.4	0.5	0	0.1	0	0.5	
1y	163.8	130.5	134.9	131.3	140.7	127.4	136.6	
2y	152.0	134.8	130.5	130.5	140.1	126.9	136.1	
	−11.8	4.3	−4.4	−0.8	−0.6	−0.5	−0.5	
1z$_1$	167.3	132.4	141.3	132.0	134.2	126.4	133.9	21.6
2z$_1$	159.2	135.6	137.2	131.2	133.7	126.1	137.1	21.3
	− 8.1	3.2	−4.1	−0.8	−0.5	−0.3	3.2	
1z$_2$	167.2	129.7	141.8	132.9	145.6	127.2	134.6	22.7, 21.5
2z$_2$	159.0	132.3	137.9	132.0	145.5	127.0	138.5	21.4, 21.4
	− 8.2	2.6	−3.9	−0.9	−0.1	−0.2	3.9	
1z$_3$	170.5	133.1	136.6	128.8	140.7	128.8	136.6	20.3, 19.3
2z$_3$	159.2	140.4	129.6	128.5	142.4	128.5	129.6	21.1, 18.8
	−11.3	7.3	−7.0	−0.3	1.7	−0.3	−7.0	
1z$_4$	171.3	140.1	127.8	134.6	133.1	134.6	127.8	19.2, 16.1
2z$_4$	160.5	145.6	125.0	134.5	133.1	135.5	125.0	19.2, 15.8
	−10.8	5.5	−2.8	−0.1	0	−0.1	−2.8	

[a] ^{19}F-N.M.R. (CDCl$_3$/C$_6$F$_{6\,int}$) *spectra:* **1w**, $\delta = 213.75$; **2w**, $\delta = 213.25$; **1x**, $\delta = 216.0$; **2x**, $\delta = 215.5$ ppm.

Table 6. Selected ^{1}H-N.M.R. (CDCl$_3$/TMS$_{int}$) Data of Alkanoyl and 2-Alkenoyl Chlorides (**1**) and Iodides (**2**), δ [ppm]

Compound	2-H[a]	3-H[a]	$\Delta\delta$(2-H)[b]	$\Delta\delta$(3-H)[b]	Other Signals
1a	2.7				
2a	3.0		0.3		
1b	4.15				
2b	4.3		0.15		
1d	2.9				
2d	3.07		0.17		
1e	3.0				
2e	3.0		0		
1q	6.1	7.1			1.95 (dd, $J = 7$ Hz, 1.5 Hz)
2q	5.8	7.0	−0.3	−0.1	1.95 (dd, $J = 7$ Hz, 1.5 Hz)
1r	—	7.2			2.0 (d, $J \approx 7$ Hz); 1.9 (s)
2r	—	7.0	—	−0.2	2.0 (d, $J \approx 7$ Hz); 1.9 (s)
1s	6.0	—			2.1 (s, 3 H); 2.0 (s, 3 H)
2s	6.4	—	0.4	—	2.0 (s, 3 H); 1.9 (s, 3 H)
1t	6.6	7.8			7.3–7.6 (5 H$_{arom}$)
2t	6.3	7.6	−0.3	−0.2	7.25–7.65 (5 H$_{arom}$)

[a] 2-H and 3-H refer to numbering of the C-chain, halocarbonyl group included. In **1q** and **2q**, the signals of 2-H and 3-H appear as precise doublets ($^3J = 15$ Hz).

[b] Chemical shift difference for 2-H, 3-H on going from acyl iodide to acyl chloride.

added to dissolve the sodium iodide. The acyl chloride (**1**; 50 mmol) is then added dropwise to the solution. The reaction starts instantaneously, as indicated by the precipitation of sodium chloride. The mixture is stirred for ~30–60 min at room temperature to ensure complete conversion.

Extraction: Pentane (redistilled from lithium alanate) is carefully poured onto the heavier acetonitrile phase until the reaction vessel is filled up to overflow and ~2/3 of the extraction flask **E** is filled with pentane. Reaction vessel **A** and the condenser are cooled with methylcyclohexane (cryostat, −25 °C), whilst the extraction is started by cautious evacuation (~150–200 torr) of the apparatus at **G**. Should there be any initial bumping of the pentane in reaction vessel **A** due to a lower pressure, the stopcock connecting vessel **A** and **E** is closed temporarily. After ~2.5 min, equilibrium is reached: The vacuum pump at **G** is turned off and the pentane begins to boil steadily in the extraction flask (which is kept at ~30 °C in a water bath), condenses in the condenser, falls through the extraction tube **B**, rises through the acetonitrile layer, and dissolves the acyl iodide, until it finally overflows and returns to the extraction flask. It takes only a little experience to assemble and grease the apparatus so that the vacuum is held without further using the pump and the extraction can be run unattended overnight.

Isolation: Cooling unit and water bath are removed, whilst the reactor-extractor is flushed with nitrogen. The product is also protected from any undesirable contact with oxygen by the cushion of gaseous pentane above the solution. The pentane in the extraction flask is evaporated and the resultant acyl iodide is dissolved in absolute dichloromethane and stored in a second smaller flask over a little copper powder as stabilizer. After evaporation of dichloromethane and flushing with nitrogen, the yield is determined (alternatively, the yield may be determined after the first evaporation of pentane from the bigger flask **E**). The acyl iodides are pure by N.M.R. standards (>95%) and may be stored neat for a few days at −20 °C with little decomposition, provided that a nitrogen atmosphere is present.

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