

Imidyl Radicals. 2 [7]

Radical Addition of *N*-Chlorophthalimide and *N*-Bromophthalimide to Alkenes

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Received September 27th, 1997, respectively December 15th, 1997

Abstract. The addition of *N*-chlorophthalimide (**1b**) to alkenes **3** via phthalimidyl radicals introduces a chlorine atom and an imidyl moiety to vicinal C-atoms of a carbon chain. The yields depend on the substituents of the alkene **3**. The regioselectivity

can be explained by steric and electronic effects; differences in the behavior of the addition of *N*-chlorophthalimide (**1b**) and *N*-bromophthalimide (**1a**) can be explained by a reversible attack of the phthalimidyl radical to the double bond.

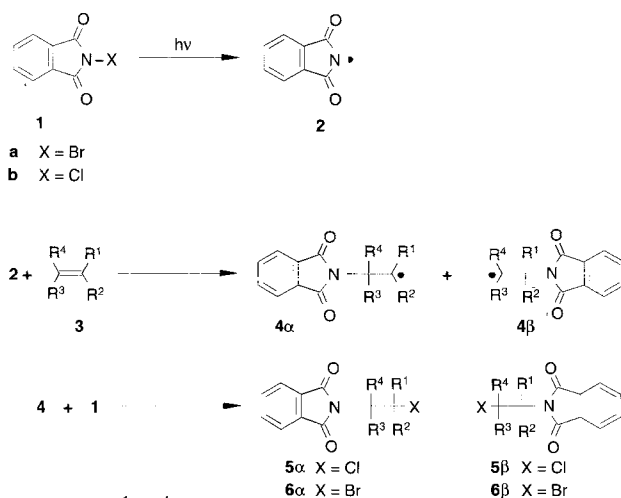
In 1942, Ziegler *et al.* [1] discovered that *N*-bromoimides (especially *N*-bromosuccinimide, NBS) can be used for highly selective allylic and benzylic brominations [2]. This radical reaction does not involve imidyl radicals [3] but is a bromine atom chain reaction. Since the discovery of imidyl radicals in 1974 [4] these imidyl radicals have been investigated intensively [5]. The main interest was focused on the structure of imidyl radicals, but it has also been shown that imidyl radicals can be used in bond forming reactions. In 1978, the first addition of *N*-bromoimides to alkenes in a radical chain reaction has been reported [6].

Since then, the radical addition of *N*-bromophthalimide (**1a**) and *N*-bromo-3,3-dimethylglutarimide to alkenes **3** has been studied in details [7]. We have now investigated whether also an *N*-chloroimide like *N*-chlorophthalimide (**1b**) can be added to alkenes *via* an imidyl radical chain, and we have therefore employed the general procedure for the addition of *N*-bromoimides to alkenes for *N*-chlorophthalimide (**1b**), too. No special reaction conditions were necessary to carry out the addition, although it was more difficult to start the chain reaction with *N*-chlorophthalimide (**1b**), probably due to the stronger N–Cl bond. To shorten the longer irradiation times, a radical initiator (AIBN or di-*tert*-butylperoxide) was added to the reaction mixture, or the addition was carried out in a quartz flask. The isolated yields of the addition products **5** are listed in table 1 and are compared to those obtained for the radical addition of *N*-bromophthalimide (**1a**) to the alkenes **3**.

As shown in table 1, the yields depend on the halogen atom and on the nature of the substituents of the alkene. In general: better yields are observed for **1a** than for **1b**. If a larger number of secondary and tertiary hydrogen atoms are present, hydrogen abstraction competes with the addition to the double bond because secondary and tertiary hydrogen atoms are abstracted rather easily. In contrast, the abstraction of hydrogen atoms from the solvent dichloromethane is slow [5b].

Regioselectivity

When *N*-haloimides **1** are added to an unsymmetrical-

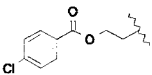


Scheme 1

ly substituted alkene (**3a–3g** and **3i–3j**), two regioisomers may be formed for **5** or **6**: one where the imidyl moiety adds in position α and the halogen in position β (**5 α** and **6 α**), and another where the imidyl moiety adds in position β and the halogen in position α (**5 β** and **6 β**). In table 2 the ratios of the regioisomers **5 α /5 β** and **6 α /6 β** are compared.

N-Bromophthalimide (**1a**) or *N*-chlorophthalimide (**1b**) generate the same phthalimidyl radical **2** and thus should give the same ratio of the radicals **4 α /4 β** . Nev-

Tab. 1 Yields for the Addition Products **5** and **6** in the Radical Addition of *N*-Chlorophthalimide (**1b**) and *N*-Bromophthalimide (**1a**) to Alkenes **3**.

Addition to 3a–k	R ¹	R ²	R ³	R ⁴	Yield (%) 5a–k ^{a)}	6a–k
a	<i>t</i> Bu	H	H	H	53	73 ^{b)}
b	<i>c</i> Hex	H	H	H	–	12 ^{a)}
c	<i>n</i> Hex	H	H	H	28	46 ^{b)}
d ^{c)}	<i>n</i> Bu	H	<i>n</i> Pr	H	39	18 ^{a)}
	<i>n</i> Bu	H	H	<i>n</i> Pr		
e	Me	Me	Me	H	34	23 ^{b)}
f	ClCH ₂	H	H	H	–	40 ^{a)}
g	OE <i>t</i>	H	H	H	11	22 ^{b)}
h	H	–(CH ₂) ₄ –		H	18	21 ^{b)}
i	H	–O(CH ₂) ₃ –		H	40	58 ^{b)}
j	Me ₃ SiO	–(CH ₂) ₄ –		H	–	6 ^{a)}
k		H	H	Et	14	26 ^{a)}

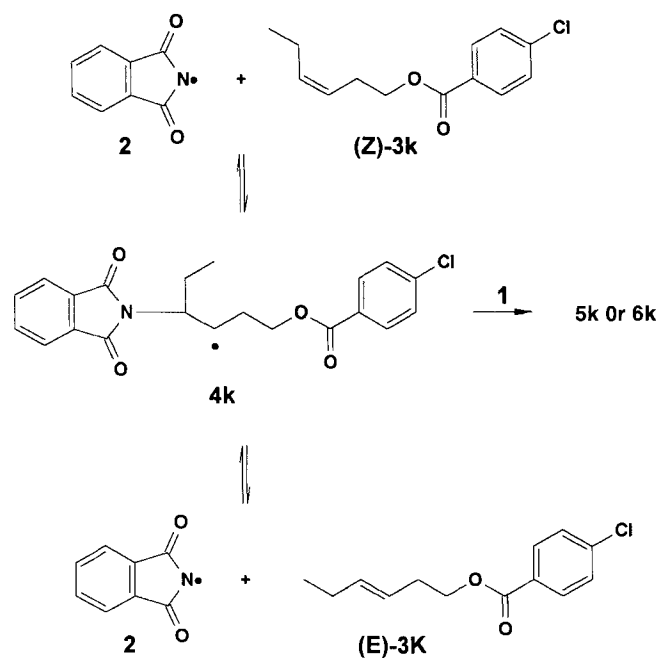
^{a)} This work. ^{b)} Ref. [7]. ^{c)} Mixture of (*E*)- and (*Z*)-non-4-ene

Tab. 2 Regioselectivity ^{a)} of the Addition of *N*-Bromophthalimide (**1a**) and *N*-Chlorophthalimide (**1b**) to Unsymmetrically Substituted Alkenes **3**.

Addition to	Analysis by	Addition of 1a 6α	6β	Addition of 1b 5α	5β
3a		> 95	< 5 ^{b)}	> 95	< 5
3b		> 95	< 5	–	–
3c		80	20 ^{b)}	> 93	< 7
	GC			21.6	19.8
3d		55	45	59	41
	NMR	4.55 4.81	4.2–4.5	4.4–4.5 4.66	4.4–4.5
3e		75	25 ^{b)}	81	19
	NMR			4.61	5.09
3f		87	13	–	–
	GC	18.4	18.0		
3g		> 95	< 5 ^{b)}	> 95	< 5
3i		> 95	< 5 ^{b)}	85	15
	NMR			5.22 4.98 (<i>trans</i>) 5.78 (<i>cis</i>)	6.08 (<i>cis</i>)
3j		> 95	< 5	–	–

^{a)} Ratios were determined either by NMR or GC. GC-conditions: SE 30/25 m, temperature program: 5 min at 100 °C, 10 °C/min to 250 °C. The ¹H NMR shift of the signals used for the determination of the regioselectivity or the GC retention times in minutes are listed in italics. When only one regioisomer could be detected, the ratio is given as > 95 : < 5. ^{b)} Ref. [7].

ertheless the ratios of the products **5 α /5 β** or **6 α /6 β** are not identical for the addition of *N*-chlorophthalimide (**1b**) and *N*-bromophthalimide (**1a**)! This fact can only be explained by a reversible addition of the phthalimidyl radical **2** to the double bond. Since the transfer of a chlorine atom from an *N*-chloroimide to a radical is slower than the transfer of bromine [8], in the chlorine case adduct radicals **4** have more time to dissociate into the alkene **3** and the phthalimidyl radical **2**, and the thermodynamically more stable adduct radicals will be formed to a larger extent (in general **4 α** is a secondary radical whereas **4 β** is a less stable primary radical). Such a reversibility was proven by adding phthalimidyl radicals **2** to (*Z*)-hex-3-enyl 4-chlorobenzoate (**3k**): if the adduct radical **4k** reacts back to the phthalimidyl radical, not only (*Z*)-hex-3-enyl 4-chlorobenzoate (**3k**) but also the thermodynamically more stable (*E*)-hex-3-enyl 4-chlorobenzoate will be formed because rotation along the former double bond is possible in the adduct radical **4k** (see Scheme 2). In fact, after addition of both *N*-chlorophthalimide (**1b**) and *N*-bromophthalimide (**1a**) to (*Z*)-hex-3-enyl 4-chlorobenzoate (**3k**) the isomeric ester could be detected in the reaction mixture by GC.



Scheme 2

With the exception of the differences in the regioisomer distribution, the radical addition of *N*-chlorophthalimide (**1b**) shows the same trend as the addition of *N*-bromophthalimide (**1a**) when added to the same alkene **3**. Steric and electronic effects are the origin of those ratios [7]. But also when two substituents R¹/R³ or R²/R⁴ are nearly the same [*n*-propyl and *n*-butyl in non-4-ene (**3d**)], a small selectivity is still found for the

less shielded position (in this case the carbon atom bearing the *n*-propyl group) for both *N*-bromophthalimide (**1a**) and *N*-chlorophthalimide (**1b**).

We thank Prof. Dr. C. Rüchardt for his generous support of this work and J. Sommer for technical assistance.

Experimental

General Information: See ref. [9]. UV Irradiations: Philips mercury lamp (125 Watt).

Materials: Dichloromethane as solvent for the reaction was dried and filtered through alumina to remove traces of acid [reaction of acid with *N*-chlorophthalimide (**1b**) generates chlorine and phthalimide], degassed in an ultrasonic bath for 15 min and saturated with nitrogen. The alkenes **3a–3c** and **3e–3i** were commercially available and have been used without further purification. **3j** was prepared as described [10].

Non-4-ene (**3d**)

was prepared by heating 35 mL (200 mmol) of nonan-5-ol [11] with 1.2 mL (6.7 mmol) of conc. H₂SO₄ to 160 °C while simultaneously distilling off the reaction product and the water formed. The emulsion was washed with 80 mL of saturated NaHCO₃ solution, and the organic layer was dried with MgSO₄. Distillation *in vacuo* at 45 °C (13 Torr) [ref. [12]: 42 °C (14 Torr)] yielded 64% of non-4-ene (**3d**).

(*Z*)-Hex-3-enyl 4-chlorobenzoate (**3k**)

was prepared by adding 10.0 g (100 mmol) of commercially available (*Z*)-hex-3-en-1-ol to a mixture of 30.6 mL (240 mmol) of 4-chlorobenzoyl chloride and 100 mL of pyridine and stirring at room temperature for 6.5 h. After distilling off excess 4-chlorobenzoyl chloride *in vacuo*, the product **3k** was distilled at 106–109 °C (0.2 Torr) yielding 69% of **3k**, $n_D^{25} = 1.5218$. – ¹H NMR (CDCl₃, TMS): δ /ppm = 1.00 (t, 7.3 Hz, 3H), 2.10 (quintet, 7.3 Hz, 2H), 2.54 (q, 6.7 Hz, 2H), 4.28 (t, 6.7 Hz, 2H), 5.46 (m_c, 2H), 7.40 (d, 8.5 Hz, 2H), 7.96 (d, 8.6 Hz, 2H). – IR (film): $\tilde{\nu}$ /cm^{–1} = 3020, 2970, 1725, 1600, 1490, 1465, 1270, 1100, 1015, 765.

C₁₃H₁₅ClO₂ calcd.: C 65.41 H 6.33 (238.71) found: C 64.77 H 6.24.

N-Chlorophthalimide (**1b**)

Chlorine was bubbled into a cold solution (0 °C) of 18.6 g (100 mmol) of potassium phthalimide [13] in 600 mL of water until a green colour persisted. After stirring for 60 min at room temperature, the white residue was filtered off, washed with cold water, dried *in vacuo* and recrystallized from tetrachloromethane, yielding 11.4 g (63%), *m. p.* 183 °C (183–185 °C [14]). – IR (KBr): $\tilde{\nu}$ /cm^{–1} = 1735, 1710, 1300, 1075, 870, 860, 710.

Radical Addition of *N*-Halophthalimides **1** to Alkenes **3** (General Procedure)

30 mmol of the alkene **3** was dissolved in 50 mL of dichloromethane. Then 3.00 mmol of *N*-halophthalimide **1** was added. Irradiation of *N*-chlorophthalimide (**1b**) was carried out in a

quartz flask, or in a Pyrex flask after addition of an initiator (AIBN or di-*tert*-butylperoxide). *N*-Bromophthalimide (**1a**) runs were irradiated in Pyrex flasks (see tables 3 and 4 for details). The mixtures were irradiated by an UV lamp (distance to the flask 1 cm). Due to the lamp heat, the reaction mixture was brought to reflux. The end of the reaction was detected by a potassium iodide-starch paper, see also ref. [5e]. Work-up procedure: *Method A.* (see tables 3 and 4 for details): after evaporation to dryness, the product was purified by column chromatography (SiO₂ and dichloromethane). – *Method B.* After evaporation to dryness, the crude product was dissolved in ca. 20 mL of dichloromethane and washed 3 times with 20 mL of sodium bicarbonate (10% in water). After drying the organic layer with magnesium sulfate, the solvent was distilled off, and the residue was recrystallized from ethanol/water (1:1).

Mass spectra of **5** and **6**

MS (EI/70 eV), m/z (%): **5a**: 265, 267 (25, 8; M⁺), 209, 211 (38, 13; M⁺–C₄H₈), 174 (10, M⁺–C₄H₈Cl), 160 (100), 148 (10), 133 (26), 130 (30), 105 (35), 104 (51), 77 (73), 76 (81); **5c**: 293, 295 (3, <3; M⁺), 257 (4), 259 (5), 174 (30), 160 (100), 148 (14), 130 (16), 105 (8), 104 (13), 77 (16), 76 (17); **5d**: 309, 307 (M⁺, <1, <1), 244 (23, M⁺–C₂H₄Cl), 230 (23, M⁺–C₃H₆Cl), 216 (50, M⁺–C₄H₈Cl), 202 (60, M⁺–C₅H₁₀Cl),

Tab. 3 Reaction Conditions, Work-up Procedure and Isolated Yields of **5** for the Addition of *N*-Chlorophthalimide (**1b**) to Alkenes **3**

Addition product	Time of irradiation (min), work-up method, glass flask and amount of initiator if added	Yield (%)
5a	630, B, Pyrex	53
5c	347, A, quartz	28
5d ^{a)}	180, A, quartz, 50 μ l of di- <i>tert</i> -butylperoxide	39
5e	720, A, quartz	17 ^{b)} 34 ^{c)}
5g	15, B, quartz	11
5h	615, B, quartz, 200 μ l of di- <i>tert</i> -butylperoxide	18
5i	60, B, Pyrex	20 ^{b)} 40 ^{c)}
5k	1580, A, quartz	14

^{a)} 1 mmol of *N*-chlorophthalimide (**1b**), 10 mmol of non-4-ene (**3d**), 15 mL of dichloromethane. ^{b)} Isolated. ^{c)} Yield by NMR.

Tab. 4 Reaction Conditions and Isolated Yields of **6** (work-up method A) for the Addition of *N*-Bromophthalimide (**1a**) to Alkenes **3**.

Addition product	Time of irradiation (min)	Yield (%)
6b ^{a)}	10	12
6d	90	18 ^{b)}
6f	60	40
6j	10 ^{c)}	6
6k	60	6 ^{d)} 26 ^{c)}

^{a)} 4.5 mmol of vinylcyclohexane (**3b**). ^{b)} Determined by NMR. ^{c)} Quartz flask. ^{d)} Isolated.

188 (59, $M^+-C_6H_{12}Cl$), 174 (81, $M^+-C_7H_{14}Cl$), 160 (100), 148 (37), 130 (59), 105 (9), 104 (19), 77 (16), 76 (24); **5e**: 215 (2, M^+-HCl), 188 (17, $M^+-C_2H_4Cl$), 174 (100, $M^+-C_3H_6Cl$), 160 (2), 148 (7), 130 (17), 77 (3), 76 (6); **5g**: 208,

210 (96, 32; $M^+-OC_2H_5$) [15], 173 (52; $M^+-OC_2H_5Cl$), 160 (11), 148 (86), 130 (100), 105 (32), 104 (45), 79 (50), 76 (71); **5h**: 265, 263 (9, 3; M^+), 228 (4, M^+-Cl), 200 (2, $M^+-C_2H_4Cl$), 186 (51, $M^+-C_3H_6Cl$), 160 (19), 148 (100), 130

Tab. 5 NMR Data of the Addition Products **5** and **6**.

Addition product	Substituent H of former alkene	N-CH _n and X-CH _n	Signals of the imidyl moiety
5a	1.13 (s, 9H)	3.90 (dd, 14.0 Hz, 3.5 Hz, 1H) 4.04 (dd, 14.0 Hz, 10.5 Hz, 1H) 4.20 (dd, 10.5 Hz, 3.5 Hz, 1H)	7.71 (m _c , 2H) 7.84 (m _c , 2H)
5c	0.86 (m _c , 3H) 1.2–1.9 (m, 10H)	3.83 (dd, 14.0 Hz, 5.3 Hz, 1H) 3.99 (dd, 14.0 Hz, 8.8 Hz, 1H) 4.28 (m _c , 1H)	7.71 (m _c , 2H) 7.85 (m _c , 2H)
5d	0.7–2.3 (m, 16H)	3.9–4.4 (m, 0.82 H) 2H β 4.4–4.6 (m, 0.59 H) 1H α 4.66 (m _c , 0.59 H) 1H α	7.74 (m _c , 2H) 7.86 (m _c , 2H)
5e	1.51 (d, 7.0 Hz, 0.51 H) β 1.64 (s, 2.49 H) α 1.70 (s, 2.49 H) α 1.72 (d, 7.3 Hz, 2.49 H) α 1.78 (s, 0.51 H) β, 1.86 (s, 0.51 H) β	4.61 (q, 7.3 Hz, 0.83 H) α 5.09 (q, 7.0 Hz, 0.17 H) β	7.7–7.9 (m, 4H)
5g	1.22 (t, 8.0 Hz, 3H) 3.62 (q, 8.0 Hz, -CH _a H _b -) 3.64 (q, 8.0 Hz, -CH _a H _b -)	4.00 (dd, 12.0 Hz, 6.0 Hz, 1H) 4.32 (dd, 12.0 Hz, 8.0 Hz, 1H) 5.54 (dd, 8.0 Hz, 6.0 Hz, 1H)	7.78 (m _c , 2H) 7.91 (m _c , 2H)
5h	1.3–2.0 (m, 6H) 2.0–2.3 (m, 1H) 2.3–2.5 (m, 1H)	4.20 (dt, J _d = 3.5 Hz, J _t = 10.5 Hz, 1H) 4.73 (dt, J _d = 3.5 Hz, J _t = 10.5 Hz, 1H)	7.73 (m _c , 2H) 7.84 (m _c , 2H)
5i	1.7–2.1 (m, 3H) 2.4–2.6 (m, 1H) 3.6–3.8 (m, 1H) 4.11 (m _c , 0.94 H) 1H of isomer A and 2 H of isomer C 4.26 (m _c , 0.11 H) 1 H of isomer B	4.36 (m _c , 0.11 H), isomer B 4.98 (ddd, 4.6 Hz, 11.3 Hz, 9.8 Hz, 0.84 H) isomer A 5.22 (d, 9.8 Hz, 0.84 H) isomer A 5.78 (d, 3.7 Hz, 0.11 H) isomer B 6.08 (d, 3.7 Hz, 0.05 H), 1H isomer C	7.76 (m _c , 2H) 7.89 (m _c , 2H)
5k	0.90 (t, 7.0 Hz, 0.46 H) 0.97 (t, 7.3 Hz, 0.92 H) 0.98 (t, 7.0 Hz, 0.46 H) 1.21 (t, 7.3 Hz, 1.15 H) 1.7–2.8 (m, 4H)	4.2–5.0 (m, 4H) ^{c)}	7.4–7.6 (m, 2H) 7.7–8.1 (m, 6H) ^{d)}
6b	1.0–2.2 (m, 11H)	3.49 (dd, 14.0 Hz, 5.3 Hz, 1H) 4.15 (dd, 14.0 Hz, 8.8 Hz, 1H) 4.39 (ddd, 8.8 Hz, 5.3 Hz, 3.5 Hz, 1H)	7.71 (m _c , 2H) 7.84 (m _c , 2H)
6d	0.7–2.4 (m, 16H)	4.2–4.5 (m, 0.82 H) 2H of β-isomer 4.55 (m _c , 0.59 H) α-isomer 4.81 (m _c , 0.59 H) α-isomer	7.74 (m _c , 2H) α + β 7.87 (m _c , 2H) α + β
6f ^{a)}		3.67 (dd, 10.5 Hz, 7.0 Hz, 0.26 H) β 3.74 (dd, 10.5 Hz, 5.6 Hz, 0.26 H) β 3.86 (dd, 10.5 Hz, 7.0 Hz, 0.74 H) α 3.98 (dd, 10.5 Hz, 5.6 Hz, 0.74 H) α 4.60 (m _c , 1 H) α + β	7.76 (m _c , 2H) α + β 7.87 (m _c , 2H) α + β
6j	0.06 (s, 1.89 H) <i>cis</i> 0.19 (s, 7.11 H) <i>trans</i> 1.3–2.5 (m, 7.79 H) 2.91 (ddd, 4.9 Hz, 12.1 Hz, 14.3 Hz, 0.12 Hz)	5.55 (q, 2.8 Hz, 0.21 H) <i>cis</i> 5.74 (dd, 3.8 Hz, 8.1 Hz, 0.79 H) <i>trans</i>	7.71 (m _c , 2H) 7.83 (m _c , 2H)
6k ^{b)}	0.87 (t, 7.5 Hz, 0.18 H) 0.91 (t, 7.5 Hz, 0.31 H) 1.04 (t, 7.2 Hz, 0.27 H) 1.16 (t, 7.2 Hz, 0.23 H) 1.6–2.9 (m, 4H)	4.1–5.1 (m, 4H) ^{c)}	7.2–7.5 (m, 2H) 7.6–8.1 (m, 6H) ^{d)}

^{a)} It was not possible to identify the hydrogen atoms of the CH-Cl and the CH-N groups. ^{b)} It was not possible to assign the 4 diastereomers. ^{c)} The N-CH_n and the Br-CH_n signals overlap with two hydrogen atoms from the alkyl moiety. ^{d)} Covered by the aromatic hydrogen atoms of the chlorobenzoyl moiety.

(28), 105 (7), 104 (18), 77 (13), 76 (24); **5i**: 229 (95, M⁺–HCl) [16], 202 (13), 201 (7), 176 (33), 173 (26), 160 (10), 148 (100), 118 (31), 105 (95), 104 (29), 77 (24), 76 (59), 75 (21); **5k**: 200 (21) [17], 188 (52), 186 (100), 160 (15), 139 (36), 130 (20), 104 (10), 76 (8); **6b**: 335, 337 (M⁺, 8, 8), 256 (M⁺–Br, 34), 160 (100), 148 (28), 130 (16), 108 (23), 104 (15), 76 (17); **6d**: 351, 353 (M⁺, 2, 2), 272 (M⁺–Br, 2), 244 (M⁺–C₂H₄Br, 20), 216 (51), 202 (56), 188 (47), 174 (55), 160 (100), 148 (37), 130 (45), 104 (25), 77 (14), 76 (24); **6f**: 301, 303 (M⁺, <1), 266, 268 (M⁺–Cl, 2, 2), 222 (M⁺–Br, 10), 187 (M⁺–ClBr, 10), 186 (M⁺–HClBr, 10), 160 (M⁺–C₂H₃BrCl, 100), 115 (11), 104 (11), 77 (10), 76 (14); **6j**: 395, 397 (M⁺, 23, 25), 380, 382 (M⁺–CH₃, 8, 7), 316 (M⁺–Br, 27), 274 (15), 248, 250 (8, 8), 233, 235 (23, 24), 220 (100), 204 (52), 160 (5), 130 (8), 77 (6), 76 (10), 75 (11), 74 (10), 73 (22); **6k**: 344 (2) [18], 342 (5), 239 (1), 237 (4), 228 (5), 188 (65), 186 (100), 160 (11), 141 (15), 139 (47), 130 (15), 113 (8), 111 (20), 104 (13), 76 (17), 75 (18).

References

- [1] K. Ziegler, A. Späth, E. Schaaf, W. Schumann, E. Winkelmann, *Liebigs Ann. Chem.* **1942**, 551, 80
- [2] L. Horner, E. H. Winkelmann, *Angew. Chem.* **1959**, 71, 349
- [3] a) J. Adam, P. A. Gosselain, P. Goldfinger, *Nature (London)* **1953**, 171, 704; b) P. A. Gosselain, J. Adam, P. Goldfinger, *Bull. Soc. Chim. Belg.* **1956**, 65, 533
- [4] a) J. G. Traynham, Y.-S. Lee, *J. Am. Chem. Soc.* **1974**, 96, 3590; b) J. C. Day, H. Lindstrom, P. S. Skell, *J. Am. Chem. Soc.* **1974**, 96, 5616
- [5] a) P. S. Skell, J. C. Day, *Acc. Chem. Res.* **1978**, 11, 381; b) U. Lüning, P. S. Skell, *Tetrahedron* **1985**, 41, 4289; c) P. S. Skell, U. Lüning, D. S. McBain, J. M. Tanko, *J. Am. Chem. Soc.* **1986**, 108, 121; d) D. D. Tanner, C. P. Meintzer, *J. Am. Chem. Soc.* **1985**, 107, 6584; e) Y. L. Chow, D.-C. Zhao, M. Kitadani, K. S.

Tab. 6 Melting Points, IR Data and Elemental Analyses for the Addition Products **5** and **6**.

Compound	Formula (molecular mass)	<i>m. p.</i> (°C)	Elemental analysis Calcd./Found	IR (KBr ^{a)}) (cm ⁻¹)
5a	C ₁₄ H ₁₆ ClNO ₂ (265.74)	97 ^{b)}	C: 62.92/63.28 H: 6.08/6.07 N: 5.18/5.27	2980, 1765, 1725, 1425, 1390, 1330, 1115, 950, 725
5c	C ₁₆ H ₂₀ ClNO ₂ (293.79)	64–66 ^{b)}	C: 65.55/65.41 H: 6.95/6.86 N: 4.68/4.77	2960, 2930, 1770, 1705, 1400, 940, 725, 715
5d	C ₁₇ H ₂₂ ClNO ₂ (307.82)	oil	HMS: ^{c)} 307.13259/307.1326	film: 2960, 2930, 2860, 1770, 1710, 1465, 730
5e	C ₁₃ H ₁₄ ClNO ₂ (251.71)	70–73 ^{d)}	C: 62.12/62.03 H: 5.59/5.61 N: 5.50/5.56	2970, 2930, 1765, 1700, 1460, 1450, 720
5g	C ₁₂ H ₁₂ ClNO ₂ (253.68)	72 ^{b)}	C: 56.64/56.82 H: 4.65/4.77 N: 5.43/5.52	2990, 2920, 1775, 1715, 1400, 1370, 1330, 1120, 1090, 1075
5h	C ₁₄ H ₁₄ ClNO ₂ (263.72)	137 ^{b)}	C: 63.50/63.76 H: 5.38/5.38 N: 5.18/5.31	2930, 2850, 1755, 1695, 1390, 1375, 1075, 1020, 950, 910, 870, 810, 800, 745, 720
5i	C ₁₃ H ₁₂ ClNO ₃ (265.70)	143 ^{d)}	C: 58.71/58.77 H: 4.65/4.55 N: 5.12/5.27	2950, 2930, 1770, 1715, 1370, 1080, 1065, 720
5k	C ₂₁ H ₁₉ Cl ₂ NO ₄ (420.29)	oil	C: 61.47/60.01 H: 4.79/4.56 N: 3.09/3.33	film: 2980, 2920, 2870, 1765, 1705, 1270, 760, 725
6b	C ₁₆ H ₁₈ BrNO ₂ (336.23)	78–80 ^{b)}	C: 56.95/57.16 H: 5.49/5.40 N: 4.03/4.17	2910, 2840, 1760, 1695, 1390, 1105, 1040, 715, 525
6d	C ₁₇ H ₂₂ BrNO ₂ (352.27)	oil	HMS: ^{c)} 351.08219/351.0822	film: 2960, 2930, 2870, 1770, 1710, 720
6f	C ₁₁ H ₈ BrClNO ₂ (302.56)	98 ^{b)}	C: 43.48/43.67 H: 2.95/3.00 N: 4.56/4.63	1770, 1700, 1390, 1110, 960, 725
6j	C ₁₇ H ₂₂ BrNO ₃ Si (396.35)	oil	HMS: ^{c)} 395.05524/395.0538	film: 2940, 2860, 1770, 1710, 1370, 1305, 1250, 1140, 725
6k	C ₂₁ H ₁₉ BrClNO ₄ (464.74)	oil	C: 54.90/54.27 H: 4.24/4.12 N: 2.76/3.01	film: 2980, 2940, 2880, 1770, 1710, 1385, 1280, 730

^{a)} If not otherwise stated. ^{b)} After evaporation of the solvent. ^{c)} High resolution mass spectrum, purity of product > 95% (NMR).

^{d)} Recrystallized from EtOH/H₂O.

- Pillay, Y. M. A. Naguib, T.-I. Ho, J. Chem. Soc., Perkin Trans 2, **1990**, 361; f) J. Lind, X. Shen, T. E. Eriksen, G. Merényi, L. Eberson, J. Am. Chem. Soc. **1991**, 113, 4629; g) P. H. Kasai, J. Am. Chem. Soc. **1992**, 114, 2875; h) J. L. Gainsforth, M. Klobukowski, D. D. Tanner, J. Am. Chem. Soc. **1997**, 119, 3339
- [6] a) J. C. Day, M. G. Katsaros, W. D. Kocher, A. E. Scott, P. S. Skell, J. Am. Chem. Soc. **1978**, 100, 1950; b) U. Lüning, D. S. McBain, P. S. Skell, J. Org. Chem. **1986**, 51, 2077
- [7] Part I: U. Lüning, A. Kirsch, Chem. Ber. **1993**, 126, 1171
- [8] J. M. Tanko, J. F. Blackert, J. Chem. Soc. Perkin Trans 2, **1996**, 1775
- [9] U. Lüning, M. Müller, Liebigs Ann. Chem. **1989**, 367
- [10] H. O. House, L. J. Czuba, M. Gall, H. D. Olmstead, J. Org. Chem. **1969**, 34, 2324
- [11] Nonan-5-ol is easily available by Grignard reaction of 1-bromomagnesiumbutane with ethylformate: R. T. Dillon, H. J. Lucas, J. Am. Chem. Soc. **1928**, 50, 1713
- [12] F. Gallais, J.-F. Labarre, C. R. Acad. Sci. **1959**, 249, 1890
- [13] For preparation of potassium phthalimide see: W. J. Hale, E. C. Britton, J. Am. Chem. Soc. **1919**, 41, 841
- [14] Beilsteins Handbuch der Organischen Chemie, 4. Ausgabe, Hauptwerk Bd. 21, Springer-Verlag, Berlin, 1918
- [15] CI-spectrum (ammonia, 170 eV): 271 (100), 273 (32) $M^+ + NH_4$.
- [16] CI-spectrum (isobutane, 170 eV): 254, 252 (34, 100, $M^+ + H$), 216 (66, $M^+ - HCl$).
- [17] CI-spectrum (isobutane, 170 eV): 424, 422, 420 (14, 70, 100, $M^+ + H$).
- [18] The mass peak was not detectable in the EI-spectrum, but the $M^+ + H$ -peak could be found in the CI-spectrum (isobutane, 170 eV): 468, 466, 464 (8, 29, 21).

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