Imidyl Radicals – Free-Radical Addition of *N*-Bromoimides to Alkenes

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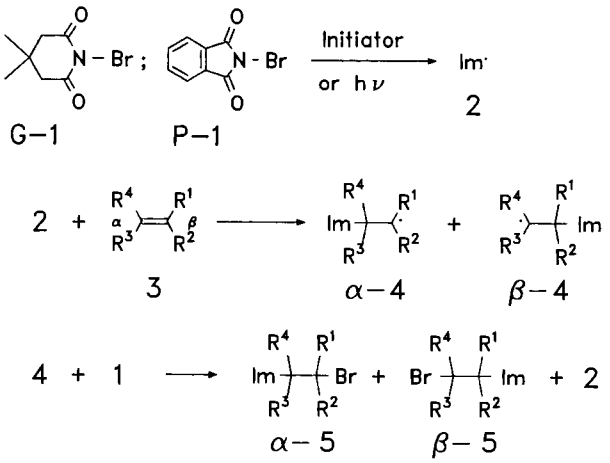
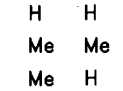
N-Bromoimides **1** add to alkenes **3** in a free-radical chain reaction on a multigram scale with imidyl radicals **2** as chain carriers. High regioselectivities are found when the substituents at the non-attacked sp^2 carbon atom to the alkene **3** are alkoxy or sterically bulky residues. The stereochemistry of the addition is determined by the bromine transfer from the *N*-bromoimide **1** to the adduct radical **4**. Formation of the *trans*-addition products **5** is favored. In competition reactions vinyl ethers react faster with the imidyl radicals **2** than alkyl-substituted alkenes.

Although *N*-bromoimides have been used in synthetic chemistry for benzylic and allylic brominations since 1942[1], imidyl radicals were not involved in these free-radical brominations[2]. They were only discovered in 1974[3]. Since then they have been investigated intensively[4], and some synthetic applications have been reported, e.g. the addition of *N*-bromoimides to alkenes in a free-radical chain reaction[5].

We have now investigated whether this addition can be carried out with normal laboratory equipment instead of using high-vacuum techniques. Furthermore, we have studied the regio- and stereochemistry of this reaction.

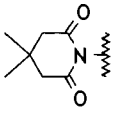
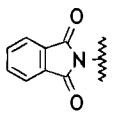
Scheme 1



3 – 6	R^1	R^2	R^3	R^4
a	*t*Bu	H	H	H
b	*n*Hex	H	H	H
c	OAc	H	H	H
d	OEt	H	H	H
e	Me	Me	Me	H
f	H	$-O(CH_2)_2-$		H
g	H	$-O(CH_2)_3-$		H
h	H	$-(CH_2)_3-$		H
i	H	$-(CH_2)_4-$		H
j	H			H
k	CH_2OH	H	H	H
l	Ph	H	H	H
m	Me	Me	Me	Me
n	Me	Me	H	H
o	Me	Cl	H	H

To carry out a free-radical addition of *N*-bromo-3,3-dimethylglutarimide (**G-1**) or *N*-bromophthalimide (**P-1**) to alkenes **3**, two requirements have to be met: the radical chain reaction must be started by light or thermally with an initiator and competing bromine radical chains (brominations according to the Goldfinger mechanism[2]) have to be suppressed (see Scheme 2). The alkenes **3** to which the imidyl radicals **2** shall be added serve as a bromine scavenger. By an ionic pathway bromine adds to the alkenes **3** and forms the dibromides **6**. The radical chain reaction may be started by irradiation of the *N*-bromoimides **1** with UV light.

For the pair *N*-bromo-3,3-dimethylglutarimide (**G-1**) / 3,3-dimethyl-1-butene (**3a**), optimization studies have been carried out in three different solvents: tetrachloromethane, acetonitrile, and dichloromethane. The irradiation time needed to complete conversion of the *N*-bromoimide **G-1**

	Im
G–1, G–2, G–4, G–5, G–8	
P–1, P–2, P–4, P–5, P–8	

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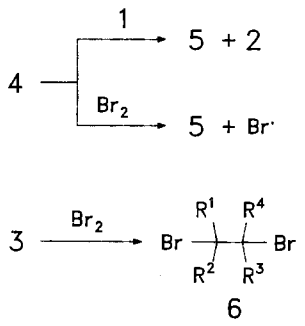
Scheme 2



depends not only on the distance between the UV lamp and the reaction vessel but also on the solvent. Typically, 10 min of irradiation (distance: 1 cm) has been sufficient for complete conversion in acetonitrile and dichloromethane. In tetrachloromethane, **G-1** is not completely soluble. Therefore, the light is partly reflected by the suspended particles leading to a longer irradiation time to achieve complete conversion. But in all cases the maximum yield of the addition product **G-5a** has been $\geq 75\%$. In all experiments, 3,3-dimethylglutarimide (**G-8**) has been found besides the addition product **G-5a**. This can be explained by hydrogen abstraction of the imidyl radical **G-2** (see Scheme 3) which adds 100 times faster to a double bond than it abstracts a primary hydrogen atom[5b]. When this selectivity is used to calculate the intramolecular competition of addition to the double bond of **3a** versus hydrogen abstraction from the *tert*-butyl group, the maximum yield for the formation of the addition product **G-5a** in tetrachloromethane is 90%. In dichloromethane, the additional possibility of hydrogen abstraction from the solvent has to be considered[4b]. Therefore, with the concentration chosen, the maximum calculated yield is 85%. The actual yields are only 10% below these calculated values.

Table 1. Isolated yields of the addition products **G-5** and **P-5** obtained from the free-radical chain addition of *N*-bromoimides **G-1** or **P-1** to alkenes **3**

Alkene 3	G-5 (Addition of G-1) (%)	Irr. time [min]	P-5 (Addition of P-1) (%)	Irr. time [min]
3a	31	120	73	95
3b	53	105	46	70
3c	-	-	22	495
3d	0 [b]	60	22	90
3e	0 [b]	90	23	10
3f	-	-	55	20
3g	-	-	58	10
3h	33 [a]	60	39	60
3i	47 [a]	60	21	120
3j	0 [b]	120	52	60
3k	-	-	0 [b]	60
3l	0 [b]	160	0 [b]	100
3m	0 [b]	135	0 [b]	135

[a] NMR yield. — [b] The reaction yielded mostly polymeric material. No addition product was found.

Table 2. Regioselectivity of the addition of phthalimidyl radicals (**P-2**) and 3,3-dimethylglutarimidyl radicals (**G-2**) to unsymmetrically substituted alkenes **3a–g**, and ^{1}H-NMR shift of those signals used for the determination of the regioselectivity. When only one regioisomer could be detected, the ratio is given as $> 95 : < 5$, and no ^{1}H-NMR shifts are listed

Addition to 3	Addition of G-2		Addition of P-2	
In position [a]	α	β	α	β
	(^{1}H-NMR shifts)			
3a	>95	<5	>95	<5
3b	60	40	80 [c]	20 [c]
	3.83	*4.10*	*3.90*	*3.65*
	4.33 [b]	*5.01*	*4.11*	*4.07*
			4.38	*4.50*
3c	>95	<5	>95	<5
3d	-	-	>95	<5
3e	-	-	75	25
			1.76	*1.70*
			1.82	*1.78*
			4.75	*5.30*
3f	-	-	87	13
			6.13	- *(cis)* [d]
			6.09	*5.43 (trans)*
3g	-	-	>95	<5

[a] α and β are defined as follows: in vinyl ethers the oxygen-substituted carbon atom of the double bound is defined as β, in all other alkenes the higher substituted carbon atom is the β position. See also Scheme 4. — [b] The signal is covered by signals of other H atoms. — [c] The regioisomers were separated. — [d] No *cis*-β-compound could be found.

Table 3. Stereoselectivity of the radical addition of *N*-bromoimides **1** to cyclic alkenes **3f–i** and ^{1}H-NMR shifts of the signals used for the determination of the stereoselectivity. In the case where only one stereoisomer was found the ratio is given as $> 95 : < 5$

Addition to	Addition of G-1		Addition of P-1	
	cis	*trans*	*cis*	*trans*
	(^{1}H-NMR shifts)			
3f	-	-	13	87
			6.13	*6.09*
3g	-	-	4	96
			5.72	*5.30*
3h	<5	>95	<5	>95
3i	38	62	27	73
	5.71	*4.73*	*5.97/5.67*	*4.27/4.88*
	6.96	*4.97*		

The reaction conditions worked out for the addition of *N*-bromo-3,3-dimethylglutarimide (**G-1**) to 3,3-dimethyl-1-butene (**3a**) have then been applied to the addition of **G-1** to other alkenes **3**. Furthermore, the type of the *N*-bromoimides used has been varied[6], *N*-bromophthalimide (**P-**

Scheme 3

1) being used as well. In Table 1 the yields of the addition products **G-5** and **P-5** for the addition of the *N*-bromoimides **G-1** and **P-1** to different alkenes **3** are listed. In all reactions, one equivalent of the *N*-bromoimide **G-1** or **P-1** and ten equivalents of the alkene **3** have been irradiated in dichloromethane until all *N*-bromoimide **G-1** or **P-1** has been consumed.

Table 1 shows that *N*-bromoimides **G-1** or **P-1** add to a variety of alkenes **3** by a radical pathway. The alkenes **3** may be mono-, di-, and trisubstituted, and they may also contain ester and ether groups. In most cases investigated, the yields for the addition of phthalimidyl radicals (**P-2**) have been higher than those for the addition of 3,3-dimethylglutarimidyl radicals (**G-2**). This may be explained by the higher selectivity κ of phthalimidyl radicals in additions to double bonds versus hydrogen abstraction [κ(**G-2**): ca. 100[5b], κ(**P-2**): ca. 1000[7]].

Table 4. Relative rates of addition κ for the addition of imidyl radicals **2** to alkenes **3**[a] and ^{1}H-NMR signals used for the determination of κ. All κ values are standardized, i. e. κ for the addition to **3a** ≡ 1.0

Alkene	Reference alkene	κ (**P-2**) (NMR of **5**) (from alkene)	κ (**P-2**) (NMR of **5**) (from reference alkene)	κ (**G-2**) (NMR of **5** (from alkene)	κ (**G-2**) (NMR of **5**) (from reference alkene)
3a	-	≡ 1.0		≡ 1.0	
3b	**3l**	2.4		2.25	
		3.82 - 4.15	*4.23/4.92 trans*	*3.81*	*4.70/4.94 trans*
		4.47	*5.68/5.86 cis*	*4.31*	*5.73/5.92 cis*
3c	[b]	1.1 [b]		2.4 [b]	
	3a	1.1		-	
		2.09/6.80	*3.95*		
3d	**3c**	12.6		-	
		5.56	*3.95/4.18/4.48*		
3n	[b]	2.6 [b]		1.4 [b]	
3o	[b]	0.95 [b]		2.3 [b]	
3e	**3i**	2.9		-	
		4.71 α	*4.22/4.90 trans*		
		5.32 β	*5.68/5.87 cis*		
3h	**3a**	1.75		1.0	
		2.51/5.78	*3.98/4.43*	*4.81/5.29*	*3.86/4.34/4.57*
3i	**3a**	2.3		2.6	
		4.92 trans	*4.50*	*4.77/5.00 trans*	*3.86/4.35/4.55*
		5.68/5.86 cis		*5.79/6.02 cis*	
3j	**3a**	2.3		-	
		4.47/5.31 exo-Im, endo-Br	*1.22*		
		5.05 exo-Im, exo-Br			
		5.91 endo-Im, exo-Br			
3f	**3d**	33.0		-	
		6.13 cis	*3.85/3.62*		
		2.39/2.96/4.97/5.56			
		6.13 trans			
3g	**3d**	7.15		-	
		5.08/5.29	*5.56*		

[a] The rates of addition were determined at different temperatures (in this work: 40 °C for the addition of **P-2**, room temp. for the addition of **G-2**; in ref.[5b]: 15 °C). In the case of the relative rate of addition to vinyl acetate (**3c**), no temperature dependence was found. — [b] Ref.[5b].

Table 5. Relative rates of the addition of electrophilic radicals[11] to alkenes **3**. All selectivities are standardized. The rate of addition to 1-butene or 1-octene (**3b**) is defined ≡ 1.0

Alkene **3**					**P-2**	**G-2**	Thiyl radicals	$Cl_3C^{\cdot}$	$Cl^{\cdot}$	$Br^{\cdot}$
R^1	R^2	R^3	R^4		(40°C)	(≈25°C)	(60°C)	(≈30°C)	(0°C)	(40°C)
Et	H	H	H		-	-	-	-	1.0	1.0
*n*Hex	H	H	H	(**3b**)	1.0	1.0	1.0	1.0	-	-
OAc	H	H	H	(**3c**)	0.46	1.1	0.81	0.8	-	-
Me	Me	H	H	(**3n**)	1.1	0.62	-	-	<1	14.5
Et	Me	H	H		-	-	1.2	0.9	-	-
H	$-(CH_2)_3-$		H	(**3h**)	0.73	0.44	0.64	0.8	-	4.7
H	$-(CH_2)_4-$		H	(**3i**)	0.96	1.2	0.25	≈0.2	0.8	-
OEt	H	H	H	(**3d**)	5.3	-	-	-	-	-
OBu	H	H	H		-	-	3.9	-	-	-

Table 6. Reaction conditions and yields of **5** for the addition of *N*-bromoimides **1** to alkenes **3**

Addition product	*N*-Bromo-imide	Alkene	Mass of **3** [g]	Time of irradiation [min]	End point determination	Solvent for chromatography (R_f) or recrystallization	Yield (%)
G-5a	**G-1**	**3a**	2.52	120	KI/starch	from petroleum ether (b. p. 30 - 50 °C)	31
G-5b	**G-1**	**3b**	3.37	105	KI/starch	CH_2Cl_2 /ethyl acetate [1 : 100] (0.86)	53
G-5h	**G-1**	**3h**	2.04	60	TLC (ethyl acetate)	ethyl acetate (0.90)	33
G-5i	**G-1**	**3i**	2.46	60	KI/starch	CH_2Cl_2 /ethyl acetate [1 : 100] (0.83)	47
P-5a	**P-1**	**3a**	2.52	95	TLC (CH_2Cl_2)	CH_2Cl_2 (0.46)	73 (41 [a])
P-5b	**P-1**	**3b**	3.37	70	TLC (CH_2Cl_2)	CH_2Cl_2 (0.57/0.55)	46
P-5c	**P-1**	**3c**	2.58	495	TLC (CH_2Cl_2)	CH_2Cl_2 (0.17)	22 (30 - 40 [a])
P-5d	**P-1**	**3d**	2.16	90	TLC (CH_2Cl_2)	CH_2Cl_2 (0.48)	22
P-5e	**P-1**	**3e**	2.10	10	TLC (CH_2Cl_2)	CH_2Cl_2 (0.64)	23
P-5f	**P-1**	**3f**	2.10	20	KI/starch	CH_2Cl_2 (0.39)	55
P-5g	**P-1**	**3g**	2.52	10	KI/starch	CH_2Cl_2 / ethyl acetate [1 : 100] (0.65 and 0.43)	58
P-5h	**P-1**	**3h**	2.04	60	TLC (CH_2Cl_2)	CH_2Cl_2 (0.77)	39
P-5i	**P-1**	**3i**	2.46	120	TLC (CH_2Cl_2)	CH_2Cl_2 (0.62)	21
P-5j	**P-1**	**3j**	2.82	60	TLC (CH_2Cl_2)	CH_2Cl_2 (0.72)	52

[a] Ref.[5b].

The addition to styrene (**3l**) has failed, only polymeric products have been isolated. Two reasons may explain this: imidyl radicals **2** may add to the aromatic ring[4b, 7, 8], and the electron density in the double bond of styrene is lower, leading to a slower addition of the electrophilic imidyl radicals **2** while simultaneously accelerating polymerization[9]. The reported polymerization of 1,1-dichloroethene[5b] may have the same reason.

For the addition of *N*-bromophthalimide (**P-1**) to 3,3-dimethyl-1-butene (**3a**) the reaction has also been carried out on a larger scale to show that this addition can also be used to generate multigram quantities of the addition products **5** [13 g (76%) of **P-5a** in a 50 mmol batch].

Regio- and Stereoselectivity

When non-symmetrically substituted alkenes such as **3a–g** are used, two regioisomeric adducts can be formed. Scheme 4 shows the two possible reaction pathways for the addition of phthalimidyl radicals (**P-2**) to 1-octene (**3b**). In this case the two regioisomers of **P-5b** have been separated by chromatography. The regioselectivity of the other additions has been determined by ^{1}H-NMR analysis. Table 2 lists their regioselectivities and the ^{1}H-NMR signals used for their determination.

Scheme 4

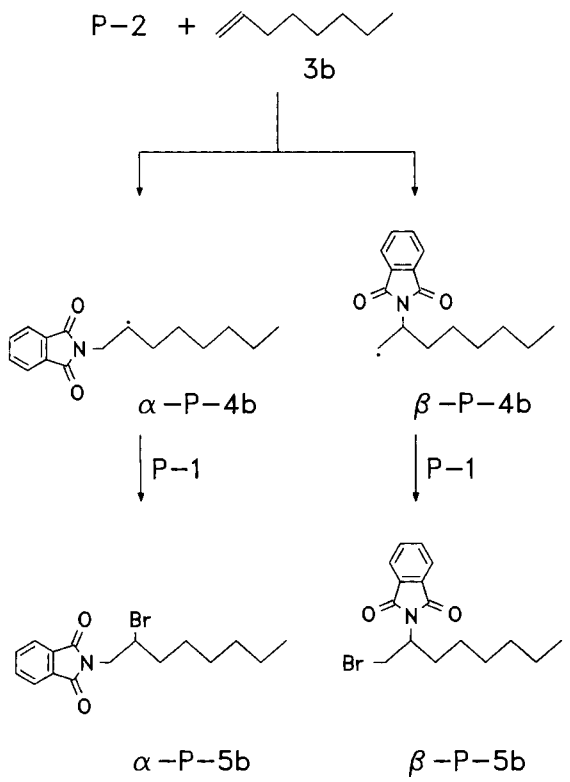


Table 2 shows that in many cases the addition of imidyl radicals **2** to alkenes **3** occurs with high regioselectivity. Two factors are responsible for this. First, a large substituent like the *tert*-butyl group in 3,3-dimethyl-1-butene (**3a**) shields the 2-position of this alkene and directs the attack to the α-position. In the case of 1-octene (**3b**) this shielding effect is smaller and hence 20% of the β-addition product have also been formed. In 2-methyl-2-butene (**3e**), the additional methyl group in the 2-position is also capable of shielding the β-position leading to a regioselectivity of 75:25. But electronic effects determine the regioselectivity of the addition as well. The steric effects of a hexyl group (in **3b**) and of an ethoxy group (in **3d**) are of the same order of magnitude. However, for ethyl vinyl ether (**3d**) only one regioisomer of the addition product **P-5d** has been found. The directing influence of oxygen atoms is also evident in the addition to vinyl acetate (**3c**) and to the cyclic ethers **3f** and **3g**. However, in the case of the five-membered dihydrofuran **3f**, two regioisomers have still been found.

While the regioselectivity of the radical addition of *N*-bromoimides **1** to alkenes **3** is established during the attack of the imidyl radical **2** on the alkene **3**, the bromine transfer from the *N*-bromoimide **1** to the adduct radicals **4** can also lead to isomers. In the case of cyclic alkenes **3** (**3f–i**), stereoisomeric addition products were formed. Table 3 lists *cis*/*trans* ratios for the additions of **G-1** and **P-1** to the cyclic alkenes **3f–i**. In all cases, the *trans*-addition has been favored[10]. However, the *cis*/*trans* ratios depend on the nature of the alkene **3** used.

Relative Rates of Addition

Relative rates of the addition of the imidyl radicals **G-2** and **P-2** to alkenes **3** have been determined in competition experiments. The alkenes **3** have been used in excess to ensure pseudo-first order behavior. By ^{1}H-NMR analysis the

Table 7. MS (EI, 70 eV) of the addition products **5**

Compound	*m/z* (%)
G-5h	331/333 (M^+, <<1), 252 (46), 142 (94), 83 (74), 55 (94), 41 (100)
P-5b	337/339 (M^+, < 1), 258 (19), 160 (100), 148 (13), 130 (19), 105 (12), 104 (18)
P-5d	297/299 (M^+, < 1), 252/254 (36), 174 (63), 204 (100), 148 (89), 130 (75), 104 (37)
P-5e	295/297 (M^+, < 1), 216 (4), 188 (18), 174 (100), 148 (14), 147 (13), 130 (31)
P-5f	295/297 (M^+, << 1), 216 (55), 188 (10), 186 (10), 148 (57), 130 (41), 41 (100), 39 (21)
P-5g	309/311 (M^+, <1), 230 (100), 160 (11), 148 (63), 130 (43), 105 (55), 104 (33), 76 (49)
P-5h	293/295 (M^+, 3), 214 (3), 169 (5), 148 (100), 130 (32)
P-5i	307/309 (M^+, 3), 228 (3), 186 (26), 160 (18), 148 (100), 130 (39)
P-5j	319/321 (M^+, 47/46), 240 (40), 160 (51), 148 (66), 130 (40), 105 (20), 104 (51), 93 (100), 77 (47), 76 (64)

Table 8. ^{1}H-NMR spectra for the addition products **5**

Addition product	MHz	Substituent *H* of former alkene	N-C*H*$_n$ and Br-C*H*$_n$	Signals of the imidyl moiety
G-5a	250	1.12 (s, 15 H) [a]	3.83 (dd, *J* = 14.0 Hz, *J* = 3.2 Hz, 1 H) 4.30 (dd, *J* = 11.4 Hz, *J* = 3.2 Hz, 1 H) 4.52 (dd, *J* = 14.0 Hz, *J* = 11.4 Hz, 1 H)	2.52 (s, 4 H) [c]
G-5b	250	0.74 - 1.86 (m, 19 H) [a]	3.83 (m, 0.6 H), 4.33 (m, 1.6 H) 4.10 (m, 0.4 H), 5.01 (m, 0.4 H)	2.51 (s, 4 H) [c]
G-5h	250	1.72 - 2.10 (m, 6 H)	4.83 (q, *J* = 8.0 Hz, 1 H) 5.29 (q, *J* = 8.0 Hz, 1 H)	1.11 (s, 6 H) 2.54 (s, 4 H)
G-5i	250	0.95 - 2.28 (m, 14 H) [a]	4.73 (td, *J* = 12.3 Hz, *J* = 3.5 Hz, 0.62 H) 4.97 (td, *J* = 12.3 Hz, *J* = 3.5 Hz, 0.62 H) 5.71 (m, 0.38 H), 6.96 (m, 0.38 H)	2.50 (s, 4 H) [c]
P-5a	250	1.21 (s, 9H)	3.95 (dd, *J* = 14.0 Hz, *J* = 3.2 Hz, 1 H) 4.18 (dd, *J* = 14.0 Hz, *J* = 10.5 Hz, 1 H) 4.48 (dd, *J* = 10.5 Hz, *J* = 3.2 Hz, 1 H)	7.74/7.88 [b]
α-P-5b	250	0.87 (t, *J* = 7.0 Hz, 3 H), 1.28 (m_C, 6 H), 1.83 (m, 2 H)	3.90 (dd, *J* = 14.0 Hz, *J* = 5.3 Hz, 1 H) 4.11 (dd, *J* = 14.0 Hz, *J* = 8.8 Hz, 1 H) 4.38 (m, 1 H)	7.71/7.87 [b]
β-P-5b	250	0.83 (t, *J* = 7.0 Hz, 3 H), 1.27 (m, 8 H), 1.81 (m, 1 H), 2.09 (m, 1 H)	3.65 (dd, *J* = 5.3 Hz, *J* = 10.5 Hz, 1 H) 4.07 (t, *J* = 10.3 Hz, 1 H) 4.50 (tt, *J* = 5.3 Hz, *J* = 15.8 Hz, 1 H)	7.74/7.87 [b]
P-5c	250	2.09 (s, 3 H)	4.24 (dd, *J* = 14.0 Hz, *J* = 5.3 Hz, 1 H) 4.35 (dd, *J* = 14.0 Hz, *J* = 7.0 Hz, 1 H) 6.81 (dd, *J* = 7.0 Hz, *J* = 5.3 Hz, 1 H)	7.76/7.90 [b]
P-5d	250	1.20 (t, *J* = 7.0 Hz, 3 H), 3.60 (q, *J* = 7.0 Hz, 2 H)	3.83 (dd, *J* = 10.5 Hz, *J* = 5.3 Hz, 1 H) 4.15 (dd, *J* = 10.5 Hz, *J* = 8.8 Hz, 1 H) 5.56 (dd, *J* = 8.8 Hz, *J* = 5.3 Hz, 1 H)	7.76/7.88 [b]
P-5e	250 400	1.70 (d, *J* = 7.0 Hz, 0.9 H), 1.76 (d, *J* = 7.0 Hz, 2.1 H), 1.78 (s, 0.9 H), 1.82 (s, 2.1 H), 1.90 (s, 3 H)	4.75 (q, *J* = 7.0 Hz, 0.7 H) 5.30 (q, *J* = 7.0 Hz, 0.3 H)	7.68 - 7.90 (m, 4 H)
P-5f	250 400	2.41 (dq, *J* = 14.0 Hz, J = 7.0 Hz, 0.87 H), 2.58 (m, 0.13 H), 2.86 (m, 0.13 H), 2.98 (dq, *J* = 14.0 Hz, *J* = 7.0 Hz, 0.87 H), 3.95 (m, 0.13 H), 4.13 (q, *J* = 6.8 Hz, 0.87 H), 4.28 (dt, *J* = 8.3 Hz, *J* = 6.8 Hz, 0.87 H, 4.45 (m, 0.13 H)	4.56 (m, 0.13 H) 4.97 (ddd, *J* = 7.5 Hz, *J* = 6.0 Hz, *J* = 4.5 Hz, 0.87 H), 6.10 (d, *J* = 4.5 Hz, 0.87 H), 6.14 (d, *J* = 6.8 Hz, 0.13 H)	7.74/7.86 [b]
P-5g [d]	250 400	1.69 (m, 1 H), 1.84 - 2.16 (m, 2 H), 2.61 (m, 1 H), 3.70 (dt, *J* = 11.4 Hz, *J* = 2.6 Hz, 1 H), 4.13 (m, 1 H)	5.08 (ddd, *J* = 12.0 Hz, *J* = 10.5 Hz, *J* = 4.5 Hz, 1 H), 5.30 (d, *J* = 10.5 Hz, 1 H)	7.74/7.88 [b]
P-5h	250	1.83 - 2.22 (m, 5 H) 2.51 (m, 1 H)	4.80 (m, 2 H)	7.74/7.86 [b]
P-5i	250	1.48 (m, 2 H) 1.70 - 2.01 (m, 4 H) 2.11 - 2.31 (m, 1 H) 2.51 (m, 1 H)	4.27 (ddd, *J* = 12.0 Hz, *J* = 10.5 Hz *J* = 3.0 Hz, 0.7 H), 4.88 (ddd, *J* = 12.0 Hz, *J* = 11.3 Hz *J* = 3.0 Hz, 0.7 H), 5.67 (m, 0.3 H), 5.97 (m, 0.3 H)	7.70/7.84 [b]
P-5j	250 400	1.24- 2.63 (m, 7.52 H) 2.70 (dd, *J* = 4.6 Hz, *J* = 1.8 Hz, 0.24 H), 3.00 (m, 0.24 H)	4.22 (d, *J* = 6.8 Hz, 0.18 H), 4.27 (dd, *J* = 6.0 Hz, *J* = 2.3 Hz, 0.7 H), 4.44 (dd, *J* = 6.8 Hz, *J* = 1.5 Hz, 0.18 H), 4.83 (t, *J* = 4.1 Hz, 0.24 H), 5.00 (ddd, *J* = 5.1 Hz, *J* = 3.8 Hz, *J* = 1.5 Hz, 0.59 H), 5.29 (dd, *J* = 4.1 Hz, *J* = 2.3 Hz, 0.24 H)	7.73/7.85 [b]

[a] The signals of the methyl groups in the glutarimidyl unit appear also at this chemical shift. — [b] The signals of the phthalimidyl system appear as AA'BB' pattern at the two given chemical shifts. — [c] The methyl signals coincide with the resonances of the substituents of the former alkene and are listed there. — [d] After chromatography, only one isomer was present.

ratio of the addition products **5** has been determined. From these data the relative rates of addition κ have been calculated. They are listed in Table 4.

From these data it is obvious that imidyl radicals **2** are electrophilic. They add to the electron-richer vinyl ethers **3d**, **f**, and **g** more readily than to the alkyl- or acetoxy-substituted alkenes **3**. A comparison of the relative rates of addition of imidyl radicals **2** with other electrophilic radicals is given in Table 5. For imidyl radicals and many other electrophilic radicals (except bromine), the selectivity towards alkyl-substituted alkenes **3** is small. Larger rates of addition have only been observed for vinyl ethers. In contrast, bromine radicals already show a very selective behavior in additions to different alkyl-substituted alkenes. If the above selectivities are compared with the selectivities in free-radical hydrogen abstractions[4b], the difference between bromine radicals and chlorine or imidyl radicals becomes obvious. All three radicals are electrophilic, but bromine is much more selective in both reactions than chlorine or imidyl radicals.

The free-radical addition of *N*-bromoimides **1** to alkyl- or oxa-substituted alkenes **3** is a suitable reaction to synthesize β-halogen-substituted, protected amines. Further studies to improve the regio- and stereoselectivities are under way.

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Experimental

General Information: See ref.[12]. – UV Irradiation: Philips mercury lamp (125 Watt).

General Procedure for the Radical Addition of N-Bromoimides **1** *to Alkenes* **3**: All solvents for the reactions were dried and filtered through alumina to remove traces of acid (reaction of acid with the *N*-bromoimides **1** generates free bromine). Then they were degassed in an ultrasonic bath for 15 min and saturated with nitrogen. – Under N_2 the reaction mixture was put into a Pyrex flask (fitted with a condenser when necessary) and placed close to the UV lamp. The alkene **3** (30 mmol) was dissolved in 50 ml of dry oxygen-free dichloromethane. Then the *N*-bromoimide **G-1** or **P-1** (3.0 mmol) was added and the mixture was irradiated by means of an UV lamp [**G-1**: distance 10 cm, room temp.; **P-1**: distance 1 cm 40°C (at 1-cm distance the lamp heated the mixture to reflux)]. The end of the reaction was determined by TLC or by a potassium iodide-starch test, see also ref.[4e]. After the solvent and excess alkene **3** had been distilled off, the crude product **5** was dried in vacuo and purified by chromatography (silica gel) or by recrystallization. Experimental details are listed in Table 6, the analytical data in Tables 7–9.

P-5b: 516 mg (1.53 mmol) of a mixture of α-**P-5b** and β-**P-5b** were purified by chromatography (silica gel, dichloromethane) yielding 322 mg (0.95 mmol) of the regioisomer α-**P-5b** and 140 mg (0.41 mmol) of the regioisomer β-**P-5b**.

α-Addition Product α-**P-5b**: M.p. 60–63°C. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.87 (t, *J* = 7.0 Hz, 3H), 1.28 (m_c, 6H), 1.61 (m, 2H), 1.83 (m, 2H), 3.90 (dd, *J* = 5.3/14.0 Hz, 1H), 4.11 (dd, *J* = 8.8/14.0 Hz, 1H), 4.38 (m, 1H), 7.71 (m, 2H), 7.87 (m, 2H). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 14.08, 22.59–36.25 (5 signals), 44.78, 52.35, 123.58, 131.91, 134.24, 168.01.

β-Addition Product β-**P-5b**: Yellow oil. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.83 (t, *J* = 7.0 Hz, 3H), 1.27 (m, 8H), 1.81 (m, 1H), 2.09 (m, 1H), 3.65 (dd, *J* = 5.3/10.5 Hz, 1H), 4.07 (t, *J* = 10.3 Hz, 1H), 4.50 (tt, *J* = 5.3/15.8 Hz, 1H), 7.74 (m, 2H), 7.87 (m, 2H). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 14.04, 22.55–32.58 (6 signals), 53.48, 123.46, 131.72, 134.16, 168.29.

Table 9. Melting points, IR data, and elemental analyses for the addition products **5**

Addition product	Formula (molecular mass)	m. p. [°C] (after chromatography)	Elemental analysis Calcd./Found	IR (KBr) [cm^{-1}]
G-5a	$C_{13}H_{22}NO_2Br$ (304.23)	94 - 96 [a]	C: 51.33 / 51.28 H: 7.29 / 7.33 N: 4.60 / 4.64	2950 , 1720, 1670 (imide), 1330, 815
G-5h	$C_{15}H_{25}NO_2Br$ (331.27)	oil	MS (for **G-5h** · H^+): Calcd.: 330.10687 Found: 330.1068	2930, 2850, 1700, 1650 (imide), 1385, 1350, 815
P-5a	$C_{14}H_{16}NO_2Br$ (310.20)	89 - 91	C: 54.21 / 54.15 H: 5.20 / 5.12 N: 4.52 / 4.47	2950, 1755, 1700 (imide), 1455, 1385, 1100, 715
P-5b	$C_{16}H_{20}NO_2Br$ (338.24)	60 - 63	C: 56.82 / 56.87 H: 5.96 / 6.03 N: 4.14 / 4.11	2900, 2830, 1760, 1690 (imide), 1390, 925, 720
P-5c	$C_{12}H_{10}NO_4Br$ (312.12)	139 - 141	[a]	2900, 1755, 1700 (imide), 1380, 1060, 700
P-5d	$C_{12}H_{12}NO_3Br$ (298.14)	76 - 78	C: 48.35 / 48.28 H: 4.06 / 4.02 N: 4.70 / 4.57	2980, 2900, 1760, 1700 (imide), 1385, 1345, 1060, 720
P-5e	$C_{13}H_{14}NO_2Br$ (296.17)	76	C: 52.73 / 52.72 H: 4.81 / 4.72 N: 4.70 / 4.73	1760, 1690 (imide), 1375, 1340, 1315, 1095, 710
P-5f	$C_{12}H_{10}NO_3Br$ (296.12)	114 - 116	C: 48.63 / 48.67 H: 3.43 / 3.40 N: 4.63 / 4.73	2930, 2830, 1760, 1705 (imide), 1455, 1360, 1055, 710
P-5g	$C_{13}H_{12}NO_3Br$ (310.15)	139	C: 50.30 / 50.35 H: 3.88 / 3.90 N: 4.46 / 4.52	2930, 2890, 1760, 1705 (imide), 1455, 1360, 1055, 710
P-5h	$C_{13}H_{12}NO_2Br$ (294.15)	129	C: 52.91 / 53.08 H: 4.06 / 4.11 N: 4.62 / 4.76	2930, 1755, 1690 (imide), 1380, 1365, 1075, 710
P-5i	$C_{14}H_{14}NO_2Br$ (308.17)	116	C: 54.57 / 54.20 H: 4.58 / 4.71 N: 4.54 / 4.33	2905, 2840, 1755, 1690 (imide), 1380, 1365, 710
P-5j	$C_{15}H_{14}NO_2Br$ (320.19)	76	C: 56.15 /56.27 H: 4.35 / 4.41 N: 4.27 / 4.37	2940, 2860, 1750, 1690 (imide), 1390, 1360, 1095, 710

[a] Ref.[5b].

P-5a *(50-mmol Scale):* 46.36 g (512.2 mmol) of 3,3-dimethyl-1-butene (**3a**) was dissolved in 800 ml of dry and oxygen-free dichloromethane. 12.94 g (57.25 mmol) of *N*-bromphthalimide (**P-1**) was added and the mixture was irradiated with an UV lamp (distance from lamp to 1-l flask: 1 cm) until all **P-1** had reacted [4.5 h, iodide starch test, TLC, silica gel/dichloromethane: R_f (**P-8**) = 0.0, R_f (**P-1**) = 0.41, R_f (**P-5a**) = 0.59]. The mixture was filtered through silica gel (10 × 5.5 cm) which was washed with 2 l of dichloromethane. Evaporation of the solvent and drying of the residue in vacuo yielded 13.44 g (43.3 mmol, 76%) of TLC-pure **P-5a**. Recrystallization from pentane yielded 9.34 g (30.1 mmol, 53%) of pure **P-5a** (microanalysis), m.p. 90–93°C.

Competition Experiments: 15 mmol of each alkene **3**[13] was dissolved in dichloromethane, then 3 mmol of the *N*-bromoimide **1** was added and the mixture was irradiated until all **1** had reacted.

After evaporation of the solvent and the alkenes **3**, ^{1}H-NMR analysis gave the relative ratio of the products **5**. Table 4 lists the alkenes and the ^{1}H-NMR signals used for the determination of the relative rates of addition κ.

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[425/92]