Imidyl Radicals. 3 [1])

Stereoselectivity of Radical Additions of *N*-Haloimides to Cyclic Alkenes

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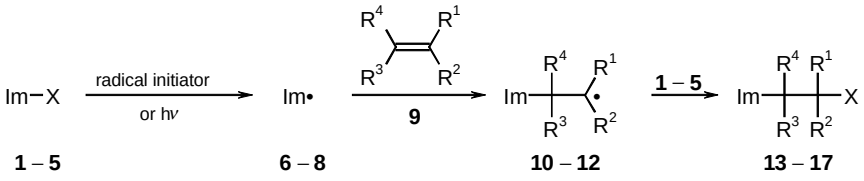
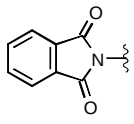
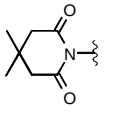
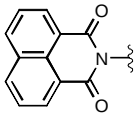
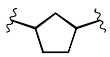
Abstract. The addition of *N*-haloimides (**1**–**5**) to alkenes **9** *via* imidyl radicals **6**–**8** introduces a halogen atom and an imidyl moiety to vicinal C-atoms of a carbon chain. With cyclic alkenes, the *trans*/*cis*-stereoselectivity depends on the nature of the imidyl unit, on the halogen atom, and on the alkene and varied between 58 : 42 and > 95 : < 5. Temperature dependend studies showed higher *trans*/*cis*-selectivities at elevated temperatures, which may be caused by different conformations of the adduct radicals **10**–**12**, each of them exhibiting a different stereoselectivity.

N-Haloimides (**1**–**5**) are used in two types of radical chain reactions: (i) the selective Ziegler bromination of allylic and benzylic positions [1], which are bromine atom chain reactions [2] and (ii) imidyl radical [3, 4] chain reactions like substitutions and especially additions to double bonds [5, 6, 7] (see scheme 1).

In this work, the addition to cyclic alkenes **9** has been investigated. Such additions may give a variety of products: regio- and stereoisomers. The regioselectivity of the radical addition of *N*-haloimides has already been studied [7]. This selectivity is determined during the first step of the radical chain when an imidyl radical **6**–



	Im	X
6, **10**		Br **1**, **13** Cl **2**, **14**
7, **11**		Br **3**, **15** Cl **4**, **16**
8, **12**		Br **5**, **17**

9-17	R^1	R^2	R^3	R^4
a	H	$-(CH_2)_3-$		H
b	H	$-(CH_2)_4-$		H
c	H	$-(CH_2)_5-$		H
d	H	$-(CH_2)_6-$		H
e	H	$-O-(CH_2)_2-$		H
f	H	$-O-(CH_2)_3-$		H
g	Me_3SiO	$-(CH_2)_4-$		H
h	H			H
i	*t*Bu	H	H	H
j	*n*Hex	H	H	H

Scheme 1. Radical addition of *N*-haloimides **1**–**5** to alkenes **9** to form addition products **13**–**17**

[1]) Imidyl Radicals. 2: see ref. [7]

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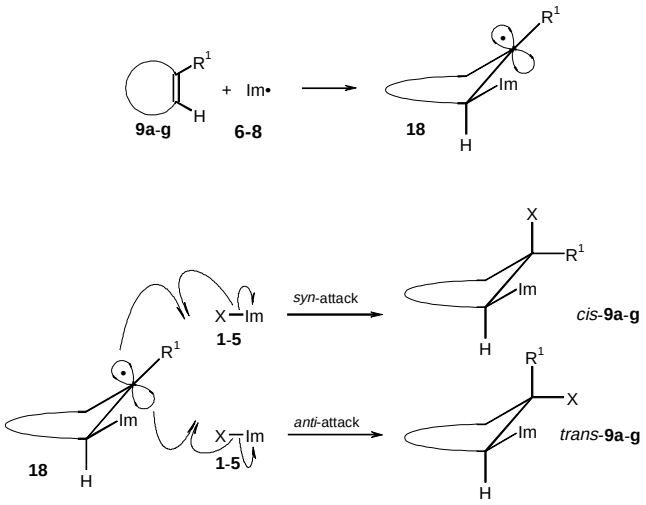
8 adds to the alkene **9** forming an adduct radical **10**–**12**. But reversible addition may lead to changes in the regioselectivity [7].

In the second step of the radical chain, the halogen atom is transfered from an *N*-haloimide **1**–**5** to the adduct radical **10**–**12**. In this transfer reaction, a second stereocenter may be established. But in contrast to the addition of the imidyl moiety to the alkene the halogen atom transfer to the adduct radicals **10**–**12** is not reversible because the radical character is lost and the non-radical products **13**–**17** are formed. With cyclic alkenes **9**, two possible orientations of this halogen atom in respect to the imidyl moiety are possible: *cis* and *trans* (see scheme 2). Both elements of an *N*-haloimide, the imidyl moiety and the halogen atom may influence the stereoselectivity.

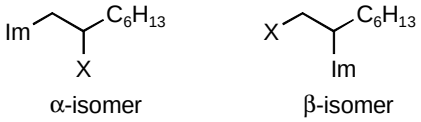


Scheme 2 The addition of imidyl radicals **1**–**5** to cycloalkenes **9a**–**g** forms adduct radicals **18**. Halogen transfer by *syn*- or *anti*-attack gives the stereoisomers *cis*-**9a**–**g** and *trans*-**9a**–**g**.

Therefore, we have investigated the stereoselectivity of the addition of five different *N*-haloimides to cycloalkenes: *N*-bromophthalimide (**1**), *N*-chlorophthalimide (**2**), *N*-bromo-3,3-dimethylglutarimide (**3**), *N*-chloro-3,3-dimethylglutarimide (**4**), and *N*-bromonaphthalene-1,8-dicarboximide (**5**). Some of the addition products **13**–**17** are literature-known, the addition of *N*-chloro-3,3-dimethylglutarimide (**4**) and *N*-bromonaphthalene-1,8-dicarboximide (**5**) to a variety of alkenes **9** yielding the addition products **16** and **17** was not studied yet. Therefore, not only the reaction of **4** and **5** with cyclic alkenes **9a**–**h** has been investigated but the addition to standard alkenes like 3,3-dimethylbutene (**9i**) and 1-octene (**9j**) has been carried out for comparison as well. As with other *N*-haloimides [7] the addition to 3,3-dimethylbutene (**9i**) only gives the α-regioisomers. But the addition of **4** and **5** to 1-octene (**9j**) gave two regioisomers as did the additions of **1**–**3**. As seen for *N*-bromo- (**1**) and *N*-chlorophthalimide (**2**), also the addition of the *N*-chloroglutarimide **4** was more selective than the addition of the bromo compound **3**. A small regioselectivity was also found for the *N*-bromonaphthalene-1,8-dicarboximide (**5**):

α/β-ratios for *N*-bromoimides: **1**: 80 : 20, **3**: 60 : 40, **5**: 67 : 33.

α/β-ratios for *N*-chloroimides: **2**: 93 : 7, **4**: 90 : 10.



All new addition products **13**–**17** have been fully characterized. In cases where microanalyses failed high resolution mass spectra (HR-MS) were recorded to prove the composition, and the purity of the compounds was checked by GC if not stated otherwise in the experimental section.

To study the stereoselectivity of the radical addition, five *N*-haloimides **1**–**5** have been treated with seven cyclic alkenes **9a**–**g** and with the bicyclic norbornene (**9h**). Table 1 summarizes the *trans*/*cis*-ratios for the addition to the cyclic alkenes **9a**–**g**, Table 2 lists the *exo*/*endo*-isomers of the additions to norbornene. The stereoselectivities were directly determined from the reaction mixtures by GC or ^{1}H NMR. During isolation, a change of the concentration of one isomer in respect to

Table 1 *trans*/*cis*-Ratios for the addition of *N*-haloimides **1**–**5** to cyclic alkenes **9a**–**g** at 40 °C, determined by GC or ^{1}H NMR. If only one isomer could be detected, >95 : <5 is listed.

addition to	**1** *trans/cis*	**2** *trans/cis*	**3** *trans/cis*	**4** *trans/cis*	**5** *trans/cis*
9a	**13a:** 92:8 [b]	**14a:** >95:<5	**15a:** >95:<5 [b]		
9b	**13b:** 92:8 [b]	**14b:** 97:3 [c]	**15b:** >95:<5 [b]	**16b:** 94:6	**17b:** >95:<5
9c	**13c:** >95:<5	**14c:** >95:<5			
9d	**13d:** 97:3	**14d:** 74:26		**16d:** >95:<5	
9e	**13e:** 87:13 [a] [b]	**14e:** 58:42 [a]			
9f	**13f:** 92:8 [a] [b]	**14f:** 64:36 [a] [c]			
9g	**13g:** 87:13 [c]				

[a]) Only α-isomer. [b]) Ref [6]. [c]) Ref [7].

Table 2 Stereoisomer distribution of the products **13h**, **14h** and **16h** obtained by the addition of *N*-haloimides **1**, **2** and **4** to norbornene (**9h**)

imidyl	halogen	**13h**	**14h**	**16h**
exo	*exo*	59	55	40
exo	*endo*	18	22	30
endo	*exo*	24	23	30
endo	*endo*	<5	<5	<5

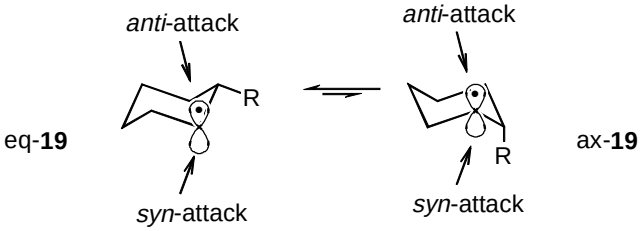
the other(s) was observed in some cases. This explains the different isomer ratios in Table **1**–**3** and in the experimental.

As Table 1 shows, in all additions the *trans*-products are favored. The selectivities vary from 58 : 42 to >95 : <5 and depend on (i) the nature of the alkene **9**, (ii) the imidyl moiety, and (iii) on the halogen atom.

Since the stereochemistry of the second stereocenter is established during the abstraction of the halogen atom by the adduct radical **10**–**12**, the transition states for this reaction step must be inspected to understand the *trans*-selectivity. In the adduct radical **10**–**12**, the first stereocenter is already formed by the addition of the imidyl radical **6**–**8** to the alkene **9**. This results in a differentiation of the two sides of the cyclus, and an attack of an *N*-haloimide will be slowed down if it occurs as a *syn*-attack rather than an *anti*-attack.

The reactions of the *N*-halophthalimides **1** and **2** with seven- or six-membered cyclic alkenes, respectively, allow to study the influence of the substituents R^1 to R^4 on the stereoselectivity and show the dependence of the *trans*/*cis*-ratios on the nature of the halogen atom, too. Eight additions have also been investigated at different temperatures: (i) the reaction of **1** with four alkenes (**9a**, **b**, **d**, **f**), and (ii) the reaction of all five *N*-haloimides **1**–**5** with cyclohexene (**9b**) (Table 3).

A decrease of the temperature has two effects on the radical additions: (i) In general, the yields drop, which suggests that competing reactions like hydrogen abstraction or chain terminations are less influenced by decreasing temperature. Reduced adducts resulting from hydrogen transfer to the adduct radicals **10**–**12** have been isolated as by-products. (ii) The stereoselectivities decrease with decreasing temperature. This is not in accord with the reactivity–selectivity principle. But the effect can be explained by two competing reactions: As stated above, the conformations of the adduct radicals **10**–**12** are important for the observed stereoselectivities (see scheme 3). Therefore, calculations have been carried out on the adduct radicals with cyclohexene **9b**. The conformations of 2-imidyl substituted cyclohexyl radicals and related ones have been calculated with different methods (see Table 4).



Scheme 3. The *trans*/*cis*-ratios of the products **13a**-**g**–**17a**-**g** are determined by the *syn*- or *anti*-attack of the *N*-haloimides **1**–**5** on the adduct radicals **19** which exist as two conformers in equilibrium, eq-**19** and ax-**19**.

In all cases calculated, the equatorial orientation of a substituent in 2-position of a cyclohexyl radical is energetically favored. But in a number of calculations the energy difference is less than 2 kcal/mol, arguing for a

Table 3 Temperature dependence of the *trans*/*cis*-product ratios obtained from the addition of *N*-haloimides **1**–**5** to cycloalkenes **9**

addition of :		**1**		**2**		**3**		**4**		**5**	
	T (°C)	*trans*/*cis*	yield (%) [a]	*trans*/*cis*	yield (%) [a]	*trans*/*cis*	yield (%) [a]	*trans*/*cis*	yield (%) [a]	*trans*/*cis*	yield (%) [a]
9a	40	92 : 8	33								
	0	94 : 6	23								
	–78	87 : 13	12								
9b	40	92 : 8	29	95 : 5	27	>95 : 5	24	94 : 6	41	>95 : 5	15
	0	89 : 11	26	–	0	>95 : 5	29	74 : 26	14	>95 : 5	14
	–78	77 : 23	20			>95 : 5	32	–	0	–	0
9d	40	97 : 3	27								
	0	87 : 13	8								
	–78	74 : 26	3								
9f	40	92 : 8	25								
	0	92 : 8	17								
	–78	94 : 6	11								

[a]) Based on *N*-haloimides **1**–**5**.

Table 4 Calculated energy differences (in kcal/mol) between the axial and equatorial conformers of 2-substituted cyclohexyl radicals **19**, and *axial*/*equatorial* ratios ax-**19** : eq-**19** calculated for 293 *K* (in parentheses).

method	substituent R				
	succinimidyl	phthalimidyl	glutarimidyl [a])	naphthalene-1.8-dicarboximidyl	phenyl-
PCM	4.68 (0:100)	5.13 (0:100)	6.14 (0:100)	5.21 (0:100)	2.71 (1:99)
AM1	1.88 (4:96)	1.87 (4:96)	2.78 (1:99)	2.79 (1:99)	1.65 (6:94)
STO-3	2.10 (3:97)	1.97 (3:97)	3.44 (0:100)	3.35 (0:100)	2.42 (2:98)
3-21G	1.12 (13:87)	1.16 (12:88)	1.94 (3:97)	1.94 (3:97)	2.51 (1:99)
6-31G*	2.32 (2:98)		2.70 (1:99)		

[a]) The glutarimidyl ring was unsubstituted in 3-position.

non-neglectable population of the axial conformer at room temperature (up to 13% in Table 4).

Therefore, at elevated temperatures the reactions of both conformers with an *N*-haloimide **1**–**5** contribute to the stereoselectivity. In the conformer ax-**19** carrying an axial imidyl substituent, a *syn*-attack will be strongly hindered and therefore this conformer will contribute to a large *trans*-selectivity. In contrast, the discrimination between *syn*- and *anti*-attack on the radical eq-**19** with the imidyl substituent in equatorial position will be smaller. If the temperature is decreased the contribution of the second stable axial conformation to the observed selectivity will decrease resulting in the smaller selectivity of the equatorial conformer.

In Table 2, the observed isomer distributions for the addition of three *N*-haloimides **1**, **2** and **4** to norbornene (**9h**) are compared. In all cases the *exo*,*exo*-isomer is favored, and the *endo*,*endo*-isomer could not be detected.

Due to the bicyclic structure the conformations of the alkene **9h** and of the adduct radicals **10h** and **11h** are not very flexible. In the first reaction step, the imidyl radical **6** or **7** can add from the *exo*- or the *endo*-side to norbornene (**9h**) forming the *exo*-adduct radicals *exo*-**10h** or *exo*-**11h**. The *exo*-attack is favored for both imidyl radicals **6** and **7**, and the *exo*-orientation of the imidyl moiety is found in 70% (**16h**) to 77% (**13h**, **14h**) of the products.

The orientation of the halogen atom is determined in the second reaction step. As in the first step, an *exo*-attack competes with an *endo*-attack but now the orientation of the imidyl substituent has an influence on the product formation as well. For the halogen transfer, the *exo*-orientation is favored even more: 70% (**16h**), 78% (**14h**) and 83% (**13h**). The *syn*- or *anti*-effect of the imidyl substituent is therefore not as important as the shielding by a methylene or an ethylene bridge in the norbornane bicyclus.

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Experimental

General Procedure for the Radical Addition of *N*-Haloimides **1**–**5** to Alkenes **9**: 30 mmol of the alkene **9** was dissolved in 50 mL of dichloromethane. Then 3.00 mmol of *N*-haloimide **1**–**5** was added. Irradiations of *N*-chloroimides (**2**, **4**) were carried out in a quartz flask, or in a Pyrex flask after addition of an initiator (AIBN or di-*tert*-butylperoxide). *N*-Bromoimide (**1**, **3**, **5**) runs were irradiated in Pyrex flasks (see tables 5–10 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. [4e]. Work-up procedure (see also tables):

Method A. After evaporation to dryness, the product was purified by column chromatography (SiO_2 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).

Method C. After evaporation to dryness, the product was dissolved in ca. 20 ml of dichloromethane and was washed three times with 20 ml of 2N NaOH. The organic layer was separated and dried with $MgSO_4$. After evaporation to dryness, the residue was either recrystallized from water/ethanol (when solid) or filtered through silica gel with ethyl acetate followed by removal of the solvent.

Table 5 Addition of *N*-haloimides **1**–**5** to alkenes **9**: irradiation times, yields and elemental analyses for **13**–**17**

	Irradiation time (min) (glassware, initiator)	Yield (%) [a] work-up method	Formula (molecular weight)	Elemental analysis found calculated %C	%H	%N
13c	20 (Duran)	13 A	$C_{15}H_{16}BrNO_2$ (322.20)	55.99 55.92	5.04 5.01	4.16 4.35
13d	150 (Duran)	35 (NMR) 21 (isolated) B	$C_{16}H_{18}BrNO_2$ (336.23)	56.88 57.16	5.26 5.40	4.15 4.17
14a [b]	1770 (Duran, air, 100 mg of AIBN)	35 A	$C_{13}H_{14}ClNO_2$ (251.71)	62.82 62.53	4.77 4.84	5.49 5.61
14c	1240 (Quartz, air, 500 µl of di-*tert*-butylperoxide)	39 (NMR) B	$C_{15}H_{16}ClNO_2$ (277.75)	64.63 64.87	5.79 5.81	4.81 5.04
14d	660 (Quartz, air, 100 µl of di-*tert*-butylperoxide)	46 (NMR) 11 (isolated) B	$C_{16}H_{18}ClNO_2$ (292.77)	HR-MS: found: 291.1016 calcd: 291.10260		
14e	40 (Quartz)	25 (NMR) 21 (isolated) A	$C_{12}H_{10}ClNO_3$ (251.67)	56.89 57.27	3.75 4.01	5.56 5.57
14h	195 (Quartz; air, 100 µl of di-*tert*-butylperoxide)	61 (NMR) 5 (isolated) B	$C_{15}H_{14}ClNO_2$ (275.73)	65.05 65.34	5.19 5.12	5.00 5.08
16b	582 (Duran, 300 µl of di-*tert*-butylperoxide)	40 D	$C_{13}H_{20}ClNO_2$ (257.76)	HR-MS: found: 257.1181 calcd: 257.11823		
16d	330 (Quartz)	25 (NMR) 13 (isolated) C	$C_{15}H_{24}ClNO_2$ (285.81)	62.83 63.08	8.34 8.40	4.84 4.90
16h [c]	95 (Duran, 50 µl of di-*tert*-butylperoxide)	40 E	$C_{14}H_{20}ClNO_2$ (269.77)	HR-MS: found: 269.1183 calcd: 269.11822		
16i	120 (Duran, 100 µl of di-*tert*-butylperoxide)	75 C	$C_{13}H_{22}ClNO_2$ (259.78)	60.03 60.11	8.44 8.54	5.38 5.39
16j	495 (Duran, 250 µl of di-*tert*-butylperoxide)	46 D	$C_{15}H_{26}ClNO_2$) (287.83)	HR-MS: found: 287.1653 calcd: 287.16519		
17b	55 (Duran)	15 (NMR) A	$C_{18}H_{16}BrNO_2$ (358.23)	59.43 60.35 [d]	4.56 4.50	3.76 3.91
17i	115 (Duran)	35 A	$C_8H_{18}BrNO_2$ (360.25)	59.96 60.01	5.01 5.04	3.79 3.89
17j	60 (Duran)	21 A	$C_{20}H_{22}BrNO_2$ (388.30)	61.44 61.86 HR-MS: found: 387.0831 calcd: 387.08340	5.71 5.71	3.61 3.48

[a]) Based on *N*-haloimides **1** – **5**. [b]) 10 mmol of **2**, 100 mmol of cyclopentene (**9a**), 150 ml of dichloromethane. [c]) 25 ml of dichloromethane. [d]) In the ^{1}H NMR spectrum, no impurities >5% were found.

Table 6 Addition of *N*-halophthalimides **1** and **2** to alkenes **9**. ^{1}H NMR data of the addition products **13**, **14** and **17** [δ (ppm), 250 MHz, $CDCl_3$, TMS].

	alkyl protons (former alkene)	-CH-Im and -CHBr (former alkene)	arene protons (former imide)
13c	1.5 – 2.0 (m, 6H) 2.1 – 2.5 (m, 4H)	4.50 (dt, J_t = 10.0 Hz, J_d = 3.0 Hz, 1H)	7.72 (m_c, 2H)
		5.98 (ddd, J = 12.0 Hz, J = 8.0 Hz,	7.85 (m_c, 2H)
	J = 4.0 Hz, 1H)		
13d [a])	1.5 – 2.1 (m, 9H) 2.1 – 2.6 (m, 3H)	4.70 (ddd, J = 2.1 Hz, J = 8.9 Hz, J = 11.0 Hz, 1H)	7.72 (m_c, 2H)
		5.16 (ddd, J = 3.1 Hz, J = 5.5 Hz, J = 11.0 Hz, 1H)	7.85 (m_c, 2H)
14a	1.9 – 2.3 (m, 5H) 2.45 (m_c, 1H)	4.73 (m_c, 2H)	7.73 (m_c, 2H)
			7.85 (m_c, 2H)
14c	1.5 – 2.4 (m, 10H)	4.37 (dt, J_d = 2.8 Hz, J_t = 10.4 Hz, 1H) 4.79 (ddd,	7.72 (m_c ,2H)
		J = 4.0 Hz, J = 8.2 Hz, J = 10.1 Hz, 1H)	7.85 (m_c, 2H)

Table 6 (continued)

	alkyl protons (former alkene)	-CH-Im and -CHBr (former alkene)	arene protons (former imide)
14d	1.3 – 2.6 (m, 12H)	4.2 – 4.4 (m, 0.6H) *cis* 4.6 (ddd, J = 10.7 Hz, J = 8.8 Hz, J = 2.1 Hz, 0.7 H) *trans* 4.95 (ddd, J = 8.7 Hz, J = 5.8 Hz, J = 2.9 Hz, 0.7 H) *trans*	7.69 (m_c, 2H) 7.81 (m_c, 2H)
14e	2.23 (dddd, J = 7.0 Hz, J = 5.2 Hz, J = 6.1 Hz, J = 13.2 Hz, 0.55H) *trans*, 2.58 (dddd, J = 3.1 Hz, J = 8.4 Hz, J = 7.0 Hz, J = 11.6 Hz, 0.45 H) *cis*, 2.79 (ddt, J_d = 10.2 Hz, J_d = 12.3 Hz, J_t = 9.1 Hz, 0.45H) *cis*, 2.95 (dq, J_q = 6.8 Hz, J_d = 13.6 Hz, 0.55H) *trans*, 3.98 (ddd, J = 7.0 Hz, J = 8.2 Hz, J = 8.9 Hz, 0.45H) *cis*, 4.16 (dt, J_d = 8.2 Hz, J_t = 6.7 Hz, 0.55 H) *trans*, 4.31 (ddd), J = 6.1 Hz, J = 7.0 Hz, J = 8.2 Hz, 0.55H) *trans*, 4.50 (ddd, J = 9.3 Hz, J = 3.2 Hz, J = 8.1 Hz, 0.45H) *cis*	4.62 (ddd, J = 8.6 Hz, J = 6.9 Hz, J = 10.2 Hz, 0.45 H) *cis* 5.01 (ddd, J = 5.1 Hz, J = 3.7 Hz, J = 7.1 Hz, 0.55 H) *trans* 5.98 (d, J = 4.0 Hz, 0.55 H) *trans* 6.17 (d, J = 7.0 Hz, 0.45H) *cis*	7.76 (m_c, 2H) 7.88 (m_c, 2H)
14h	1.2 – 1.9 (m, 4H) 1.9 – 2.2 (m, 1H) 2.2 – 2.7 (m, 2.89H) 3.0 – 3.0 (m, 0.11H)	4.11 (dd, J = 2.4 Hz, J = 5.5 Hz, 0.58H) [c] 4.25 (m_c, 0.22 H) [d] 4.61 (t, J = 4.0 Hz, 0.31H) [e] 4.97 (m_c, 0.58H) [c] 5.25 (dd, J = 3.7 Hz, J = 2.1 Hz, 0.31H) [e]	7.73 (m_c, 2H) 7.87 (m_c, 2H)
17b	1.4 – 1.6 (m, 2H) 1.7 – 1.9 (m, 1H) 1.9 – 2.1 (m, 3H) 2.4 – 2.6 (m, 2H)	5.27 (m_c, 2H)	7.77 (dd, J = 8.2 Hz, J = 7.3 Hz, 2H) 8.22 (dd, J = 1.2 Hz, J = 8.2 Hz, 2H) 8.60 (m_c, 2H)
17i [f]	1.25 (s, 9H)	4.30 (dd, J = 14.0 Hz, J = 3.0 Hz, 1H) 4.62 (dd, J = 11.0 Hz, J = 3.0 Hz, 1H) 5.02 (dd, J = 14.0 Hz, J = 11.0 Hz, 1H)	7.78 (dd, J = 9.0 Hz, J = 7.0 Hz, 2H) 8.26 (dd, J = 9.0 Hz, J = 1.0 Hz, 2H) 8.64 (dd, J = 7.0 Hz, J = 1.0 Hz, 2H)
17j [b]	0.84 (m_c, 3H) 1.1 – 1.5 (m, 8H) 1.74 (m_c, 1H) 1.89 (m_c, 2H)	4.36 (dd, J = 6.0 Hz, J = 13.0 Hz, 1H) 4.54 (m_c, 1H) 4.75 (dd, J = 8.0 Hz, J = 13.0 Hz, 1H)	7.74 (dd, J = 8.0 Hz, J = 7.0 Hz, 2H) 8.21 (dd, J = 8.0 Hz, J = 2.0 Hz, 2H) 8.59 (dd, J = 7.0 Hz, J = 2.0 Hz, 2H)

[a]) Only the *trans*-**13d** was isolated. [b]) The pure isolated product was the α-**17j**. In the crude ^{1}H NMR 33% of β-**17j** was found (δ = 4.16). [c]) *exo*-Imidyl, *exo*-Cl. [d]) *exo*-Imidyl, *endo*-Cl. [e]) *endo*-Imidyl, *exo*-Cl. [f]) Only one regioisomer was found in the ^{1}H NMR.

Table 7 Addition of *N*-chloro-3,3-dimethylglutarimide (**4**) to alkenes **9**. ^{1}H NMR data of the addition products **16** [δ (ppm), 250 MHz, $CDCl_3$, TMS].

Nr.	alkyl protons (former alkene)	-CHIm- und -CHCl- (former alkene)	CH_2 (former imide)	CH_3 (former imide)
16b	1.2 – 2.3 (m, 8H)	4.66 (ddd, J = 12.0 Hz, J = 11.3 Hz, J = 3.9 Hz, 1H) *trans*, 4.80 (dt, J_t = 11.1 Hz, J_d = 4.4 Hz, 1H) *trans*, 5.7 – 5.8 (m, 1H) *cis* 5.9 - 6.1 (m, 1H) *cis*	2.50 (s, 4H)	1.10 (s, 6H)
16d	1.4 – 1.8 (m, 8H) 1.9 – 2.1 (m, 2H) 2.1 – 2.4 (m, 2H)	4.95 (ddd, J = 11.0 Hz, J = 5.65 Hz, J = 2.9 Hz, 1 H) 5.17 (ddd, J = 10.7 Hz, J = 7.9 Hz, J = 1.4 Hz, 1H)	2.51 (m_c, 4H)	1.07 (s, 3H) 1.15 (s, 3H)
16h	1.1 – 2.7 (m, 18H) [a]	4.24 (d, J = 6.8 Hz, 0.3H) [b] 4.34 (d, J = 6.8 Hz, 0.3H) [b] 4.59 (dd, J = 2.0 Hz, J = 6.8 Hz, 0.4H) [c] 4.86 (m_c, 0.7H) [a] [c] 5.23 (dd, J = 2.0 Hz, J = 3.8 Hz, 0.3H) [d]	[a])	[a])
16i	1.11 (s, 9H)	3.80 (dd, J = 14.0 Hz, J = 3.2 Hz, 1H) 4.13 (dd, J = 10.5 Hz, J = 3.2 Hz, 1H) 4.42 (dd, J = 14.0 Hz, J = 10.5 Hz, 1H)	2.52 (s, 4H)	1.13 (s, 6H)
16j [e]	0.88 (m_c, 3H) 1.1 – 1.8 (m, 16H)	3.77 (dd, J = 12.3 Hz, J = 3.5 Hz, 1H) α 4.2 – 4.3 (m, 2H) α 3.63 (dd, J = 11.3 Hz, J = 5.3 Hz, 1H) β 4.0 – 4.1 (m, 2H) β	2.53 (s, 4H) α+β	1.12 (s, 6H) α+β

[a]) The alkyl protons of the former norbornene and the proton of the imidyl moeity overlap. [b]) *exo*-Imidyl, *endo*-Cl. - c) *exo*-Imidyl, *exo*-Cl. - [d]) *endo*-Imidyl, *exo*-Cl. [e]) The crude reaction mixture contained 90 % of the α-regioisomer α-**16j** and 10 % of the β-regioisomer β-**16j**.

Table 8 Addition of *N*-Haloimides **1**–**5** to alkenes **9**. Chromatography details, melting points and MS data of the addition products **13** – **17**

	chromatography (SiO_2/CH_2Cl_2), R_f	*m. p.* (°C)	*m/z* (%) (EI, 70 eV)
13c	A, 0.65	99 – 101 [a])	321, 323 (M, 10, 10), 242 (M–Br, 42), 186 (45), 160 (34), 148 (100), 130 (37), 105 (14), 104 (42), 95 (51), 76 (44)
13d	B	76 (EtOH/H_2O)	335, 337 (M, 5, 5), 256 (M–Br, 21), 186 (M–C_5H_{10}Br, 59), 173 (M–C_7H_{12}Br, 13), 160 (39), 148 (100), 130 (35), 104 (26)
14a	B	133 (EtOH/H_2O)	249, 251 (14, 4; M), 186 (M-C_2H_4Cl), 160 (8), 148 (100), 130 (40), 105 (10)
14c	A, 0.78	83 [a])	277, 279 (22, 7, M), 242 (6, M–Cl), 186 (100, M–C_4H_8Cl), 173 (9, M–C_5H_9Cl), 160 (36, M–C_6H_{10}Cl), 148 (95, M–C_7H_{10}Cl), 130 (54), 105 (17), 104 (44)
14d	A, 0.82	55 – 58 [a])	291, 293 (17, 6, M), 256 (6, M–Cl), 186 (75, M–C_5H_{10}Cl), 173 (23, M–C_6H_{11}Cl), 160 (35), 148 (100), 130 (37), 108 (31), 104 (29)
14e	A, 0.62 and 0.57 (isomers)	95 [a])	215 (49, M–HCl) [b]), 187 (37, M–C_2H_5Cl), 186 (26, M–C_2H_6Cl), 148 (83, C_4H_4ClO), 130 (88), 105 (34), 104 (33), 41 (100)
14h	A, 0.7	112 [a])	275, 277 (100, 37, M), 276 (38), 274 (36), 241 (15, M+H–Cl), 240 (15, M–Cl), 239 (13, M–HCl), 211 (47, M–C_2H_5Cl), 200 (15, M–C_3H_4Cl), 186 (23, M–C_4H_6Cl), 172 (36, M–C_5H_8Cl), 160 (41), 148 (57), 130 (25), 105 (6), 104 (28)
16b	D	yellow oil	221 (3, M–HCl), 142 (100, M–C_6H_8Cl), 114 (18, M–C_7H_8ClO)
16d	C	94 (EtOH/H_2O)	285, 287 (2, <1, M), 250 (16, M–Cl), 180 (7, M–C_5H_{10}Cl), 142 (100, M–C_8H_{12}Cl), 114 (23), 83 (57)
16h	E, 0.68	colorless oil	287, 289 (36, 100, M+NH_4) [c]), 270, 272 (63, 20), 234 (63)
16i	C	110 – 115 (EtOH/H_2O)	259, 261 (11, 4, M), 203, 205 (22, 8, M–C_4H_8), 168 (26, M–C_4H_8Cl), 154 (24), 151 (34), 136 (100), 108 (32), 83 (56)
16j	D	yellow oil	287, 289 (2, 1, M), 252 (7, M–Cl), 154 (11, M–C_7H_{14}), 142 (100, M–C_8H_{14}Cl), 126 (13), 83 (53)
17b	A, 0.57	177	357, 359 (8, 8, M), 198 (100), 180 (12), 152 (6)
17i	A	160 [d])	359, 361 (28, 29, M), 280 (9, M–Br), 224 (9, M–C_4H_9Br), 210 (59, M–C_5H_{10}Br), 197 (100, M–C_6H_{12}Br)
17j	A, 0.55	82	387, 389 (11, 11, M), 308 (44, M–Br), 210 (55), 198 (100), 197 (74), 180 (41), 152 (20)

[a]) After evaporation of the solvent. b) No mass peak in the EI spectrum, but the CI spectrum (isobutane) showed M+CH_3: 266 (100), 268 (11). [c]) CI-Spektrum (ammonia, 170 eV). [d]) Ref [8]: 126 – 127 °C.

Table 9 IR data of the addition products **13**, **14**, **16** and **17**

		ν (cm^{-1})
13c	KBr	1765 (m), 1710 (s), 1395 (s), 1380 (s), 1355 (s), 730 (s)
13d	KBr	1765 (s), 1710 (vs), 1395 (s), 1385 (s), 1365 (s), 1115 (s), 730 (vs)
14a	KBr	1770 (m), 1705 (s) 1090 (m), 730 (s)
14c	KBr	1765 (m), 1705 (s), 1390 (s), 1380 (s), 725 (s)
14d	KBr	1770 (m), 1710 (s), 1380 (s), 1120 (m), 1090 (m), 725 (s).
14e	KBr	1770 (m), 1720 (s), 1375 (s), 1060 (s), 725 (s)
14h	KBr	1765 (s), 1710 (vs), 1375 (s), 1110 (s), 720 (s)
16b	film	1730 (m), 1670 (s), 1460 (m), 1400 (m), 1360 (m), 750 (m)
16d	KBr	1715 (m), 1685 (s), 1355 (s), 1275 (s), 1235 (s), 640 (m), 610 (m)
16h	film	1730 (m), 1680 (s), 1460 (m), 1420 (m), 1360 (m), 640 (m)
16i	KBr	1723 (m), 1675 (s), 1360 (m), 1145 (m), 630 (m)
16j	film	1730 (m), 1680 (s), 1360 (m), 680 (m), 630 (m)
17b	KBr	1695 (s), 1655 (s), 1340 (s), 1240 (s), 785 (s)
17i	KBr	1645 (s), 1575 (s), 1315 (s), 1225 (s), 935 (m), 765 (s)
17j	KBr	1700 (s), 1660 (s), 1650 (s), 1385 (s), 1360 (s), 1335 (s), 1240 (s), 1175 (s), 770 (vs)

Table 10 Stereoselectivity of the radical addition of *N*-Haloimides **1** – **5** to cyclic alkenes **9a** – **h**. The selectivities were determined from the crude reaction mixtures by GC and ^{1}H-NMR. The retention times and the chemical shift used for the determination of the stereoselectivity are listed.

	GC or ^{1}H-NMR	*trans*-product	*cis*-product
		r_t (min) or δ (ppm)	
13c	^{1}H-NMR	only *trans*-product in ^{1}H-NMR	
13d	GC	91 *19.3 min*	9 *20.0 min*

Table 10 (continued)

	GC or ^{1}H-NMR	*trans*-product	r_t (min) or δ (ppm)	*cis*-product
13g [a])	^{1}H NMR	87		13
		5.74 ppm		*5.55* ppm
14a	^{1}H NMR		only *trans*-isomer	
14b	^{1}H NMR	97		3
		4.20, 4.73		*5.6 – 5.8, 5.9 – 6.1*
14c	^{1}H NMR		only *trans*-isomer	
14d	^{1}H NMR	74		26
		4.57, 4.95		*4.2 – 4.4*
14e	^{1}H NMR	58		42
		5.98		*6.17*
14f	^{1}H NMR	64		36
		4.98, 5.22		*5.78*
16b	^{1}H NMR	94		6
		4.66, 4.80		*5.7 – 5.8, 5.9 – 6.1*
16d	^{1}H NMR		only *trans*-isomer	
17b	GC [b])		only one isomer	

[a]) Ref. 7. [b]) GC-conditions: DB 1/25 m, 5 min at 100 °C, 10 °C/min until 250 °C, 20 min at 250 °C.

Method D. See method C, but 20 ml of diethyl ether was used to dissolve the crude product.

Method E. See method A, but ethyl acetate/dichloromethane (9:1) was used for chromatography. – In some cases the material was purified twice to obtain analytically pure material (see Table 8 for details).

References

[1] a) K. Ziegler, A. Späth, E. Schaaf, W. Schumann, E. Winkelmann, Liebigs Ann. Chem. **1942**, *551*, 80; b) L. Horner, E. H. Winkelmann, Angew. Chem. **1959**, *71*, 349

[2] 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

[3] First publications on imidyl radicals: 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

[4] 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. 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; i) G. Merényi, J. Lind, L. Eberson, Acta Chem. Scand. **1998**, *62*, 62

[5] 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

[6] U. Lüning, A. Kirsch, Chem. Ber. **1993**, *126*, 1171

[7] A. Kirsch, U. Lüning, J. prakt. Chem. **1998**, *340*, 129

[8] J. C. Day, N. Govindaraj, D. S. McBain, P. S. Skell, J. M. Tanko, J. Org. Chem. **1986**, *51*, 4959

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