

# Relative Intramolecular Reactivity of the Insulated $\pi$ Double Bond and the $14\pi$ Annulene Perimeter toward Sulfur Trioxide in the Sulfonation of Isopyrenes<sup>[\*]</sup>

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Received July 16, 1996

**Keywords:** Sulfur trioxide sulfonation / [14]Annulene / [14]Annulenemono- and -disulfonic acids /  $\beta$ -Sultone and carbyl sulfate (pyrosultone) formation

The sulfonation of isopyrene (**1**) and its 5-methyl- and 5,10-dimethyl derivative **2** and **3** with  $\text{SO}_3$  in both dichloromethane and nitromethane as solvent has been studied. Reaction of **1** and **2** leads to sulfodehydrogenation in which  $\text{SO}_3$  reacts as a monodentate electrophile, the initial products being 1-5-sulfonic acid (1-5-S) and 2-10-S, respectively. In the presence of a sufficiently large amount of  $\text{SO}_3$  1-5-S is subsequently converted into 1-5,10-S<sub>2</sub>. With **3**, using 2.0 mol-

equiv. of the sulfonating reagent in dichloromethane, the  $\text{SO}_3$  adds as a bidentate electrophile to the "central C=C bond" with formation of 7,14-dimethyl-1,6:8,13-ethanediylidene-[14]annulene-15,16-sultone (**5**) and the corresponding pyrosultone **6**. Upon subsequent hydrolysis and neutralization with aqueous KOH the eventually obtained product is potassium 16-hydroxy-7,14-dimethyl-1,6:8,13-ethanediylidene-[14]annulene-15-sulfonate (**4**).

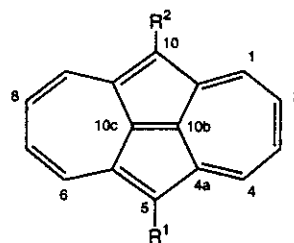
## Introduction

Sulfonation using the dioxane- $\text{SO}_3$ <sup>[1]</sup> and pyridine- $\text{SO}_3$ <sup>[2]</sup> complexes is in general more rapid with alkenes than with simple aromatic hydrocarbons. For intermolecular competition of 1-hexadecene and dodecylbenzene the sulfonation rate coefficient ratio  $k_{\text{alkene}}/k_{\text{alkylbenzene}} = 130$ <sup>[3]</sup>. This is in line with the value of  $\geq 100$  reported for the intramolecular competition for the  $\text{SO}_3$  sulfonation of non-conjugated  $\omega$ -phenylalkenes<sup>[4]</sup>.

Sulfonation of an alkene with an equimolar amount of  $\text{SO}_3$  yields initially a  $\beta$ -sultone<sup>[5,6]</sup>. Upon using an excess of  $\text{SO}_3$  the  $\beta$ -sultone is converted into the corresponding pyrosultone (also referred to as carbyl sulfate or cyclic sulfonate sulfate anhydride)<sup>[7-9]</sup>. For a number of substrates these two types of sulfo products could in fact be isolated<sup>[7,8]</sup>, especially when starting with fluorinated alkenes<sup>[10,11]</sup>. However, even upon rapidly working up pyrosultone reaction mixtures under hydrolytic conditions, in general a mixture of the corresponding  $\beta$ -hydroxyalkanesulfonic acid and  $\alpha$ -alkene- $\gamma$ -sulfonic acid is obtained<sup>[12,13]</sup>.

In relation to the problem of the relative intramolecular reactivity of different  $\pi$ -electron systems we have studied before the sulfonation of 11-methylene-1,6-methano[10]annulene of which the insulated C(11)=C(12)  $\pi$ -bond and the

Hückel  $10\pi$  electron system in the perimeter are essentially orthogonal<sup>[14]</sup>. The initial sulfonation of 11-methylene-1,6-methano[10]annulene occurs exclusively at one of the  $\alpha$ -positions of the ring<sup>[15]</sup>; the formation of the 12,11-sultone becomes competitive not until the 11-methylene-1,6-methano[10]annulene-2-sulfonic acid is formed<sup>[14]</sup>. As an extension, we now report on the sulfonation of isopyrene (**1**) and its 5-methyl- and 5,10-dimethyl derivative **2** and **3**. X-ray crystallographic analysis<sup>[17,18]</sup> and spectroscopic studies<sup>[19]</sup> illustrate that isopyrene (**1**) is planar and that the dominant mesomeric structures are **1a** and **1b**, having a conjugative  $14\pi$  electron perimeter and a planar bridging C(10b)=C(10c) unit<sup>[20]</sup>, in agreement with calculated average bond orders<sup>[22]</sup>.



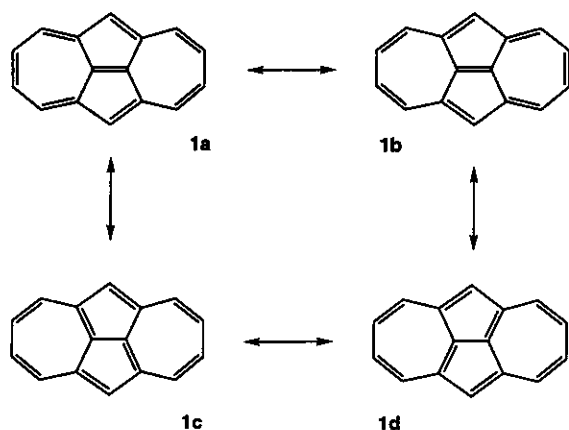
- 1  $R^1 = R^2 = \text{H}$
- 2  $R^1 = \text{Me}; R^2 = \text{H}$
- 3  $R^1 = R^2 = \text{Me}$

Gleiter and Vogel<sup>[23]</sup> have stressed that isopyrene (**1**) exhibits ambident behaviour towards electrophiles. Standard

[◇] Part 129: H. Cerfontain, A. Koeberg-Telder, R. H. Mitchell, N. Khalifa, M. Tashiro, *Recl. Trav. Chim. Pays-Bas* **1996**, *115*, 293-301.

[\*] IUPAC name of isopyrene: Azuleno[2,1,8-*ija*]azulene.

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Hückel MO calculations on **1**<sup>[22]</sup> have shown the highest electron density to be on C(5) and C(10), and hence lead to the prediction that monodentate electrophiles will preferentially attack **1** at these two positions. On the other hand the HOMO of **1** possesses significant orbital coefficients, not only at C(5) and C(10), but also at C(10b) and C(10c). Accordingly, the reaction of **1** with a bidentate electrophile via a cyclic transition state should occur at both C(10b) and C(10c), since the simultaneous interaction of the reagent with the 2p orbitals at these two carbon atoms will make two contributions of equal magnitude to the energy instead of only one, as would be the case when the electrophile attacks as monodentate at either C(5) or C(10)<sup>[23]</sup>. In fact, reaction of **1** with trifluoroacetic acid does lead to protonation at C(5), forming a stable carbenium ion<sup>[24]</sup>, and the chlorination<sup>[25]</sup>, bromination<sup>[25,26]</sup>, iodination<sup>[25]</sup> and chloromercuriation<sup>[27]</sup> of **1** lead to substitution with formation of the corresponding 5,10-dihalogenoisopyrenes and 5,10-bis(chloromercurio)isopyrene, respectively. On the contrary, reaction of **1** with ozone, osmium tetroxide and

peracetic acid leads to addition of these bidentate electrophiles to the central C(10b)=C(10c) bond<sup>[23]</sup>.

Sulfur trioxide is known to react both as monodentate (with e.g. alkanols<sup>[1]</sup> and simple arenes<sup>[28]</sup>, leading to *O*- and *C*-sulfonation respectively), and as bidentate electrophile (with e.g. alkenes, leading in a concerted fashion to the formation of  $\beta$ -sulfones<sup>[5,6]</sup>). In view of the dualistic reactivity behaviour of both isopyrene and SO<sub>3</sub> we have studied their mutual reaction in some detail.

## Results

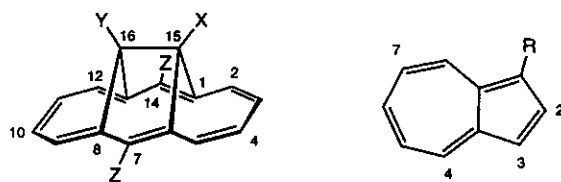
The reactions of the isopyrenes **1–3** with SO<sub>3</sub> were studied in dichloromethane as inert solvent in the absence and presence of 1,4-dioxane as reactivity moderator at  $-30$  to  $17^\circ\text{C}$ , and also in the SO<sub>3</sub>-complexing solvent nitromethane<sup>[29]</sup> in the temperature range of  $-30$  to  $25^\circ\text{C}$ . In nitromethane the solubility of isopyrene (**1**) is limited, rendering the reaction mixtures heterogeneous when using this solvent. The reaction mixtures were worked up by addition of an excess of water, followed by neutralization with aqueous KOH. The compositions of the various reaction product mixtures in the kinetically controlled<sup>[30]</sup> sulfonations with SO<sub>3</sub> were determined by <sup>1</sup>H-NMR multicomponent analysis on the basis of the specific absorptions of the various components<sup>[31]</sup>. The results are compiled in Table 1.

Monosulfonation of isopyrene (**1**) with SO<sub>3</sub> in dichloromethane as solvent, both in the absence and presence of 1.1 mol-equiv. of dioxane relative to the amount of SO<sub>3</sub> as reactivity moderator, leads to the formation of isopyrene-5-sulfonic acid (**1-5-S**) as the only detectable product. Further sulfonation (Scheme 1) yields **1-5,10-S<sub>2</sub>** (Table 1, entries 4–6). Upon sulfonation with 2.0 and 4.0 mol-equiv. of SO<sub>3</sub> in nitromethane as solvent the same disulfonic acid is obtained as the only product (entries 1 and 2). 5-Methylisopyrene (**2**) upon reaction with SO<sub>3</sub> in dichloromethane affords

Table 1. Sulfonation of the isopyrenes **1–3** with SO<sub>3</sub> in various solvent systems

Entry	Substrate	Reaction conditions				Method of reaction and analysis	Reaction mixture composition (% $\pm$ 2)				Material balance (%)	
		SO <sub>3</sub> equiv.	Solvent <sup>[a]</sup>	T [°C]	time [h]		Unconverted substrate	1-5-SO <sub>3</sub> X	1-5,10-(SO <sub>3</sub> X) <sub>2</sub>	2-10-SO <sub>3</sub> X		4
1	<b>1</b>	2.0	N	25	0.25	A	-	-	90	-	-	90
2	<b>1</b>	4.0	N	25	0.25	A	-	-	90	-	-	90
3	<b>1</b>	1.0	D/DCM (1:100, v/v)	-30	0.25	B	62	38	-	-	-	100
4	<b>1</b>	2.0	D/DCM (1:100, v/v)	-20	4.0	C	40	40	11	-	-	91
5	<b>1</b>	4.0	D/DCM (1:1, v/v)	17	0.25	D	8	4	71	-	-	83
6	<b>1</b>	2.0	[D <sub>2</sub> ]DCM	-25	0.25	E	23	37	30	-	-	90
				-20	4.0		-	29	37	-	-	66
7a	<b>2</b> <sup>[c]</sup>	2.0	DCM	-30 $\rightarrow$ 0	5.0	E	-	-	-	8	-	42
7b	<b>+3</b>						26	-	-	-	52	96

<sup>[a]</sup> N, D and DCM stand for nitromethane, dioxane and dichloromethane, respectively. – <sup>[b]</sup> For entry 6, X stands for H; for all other entries, X stands for K. – <sup>[c]</sup> The molar composition ratio of the mixture of **2** and **3** is 19:81.

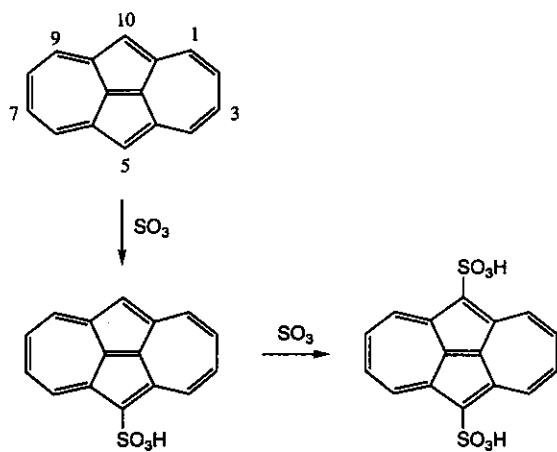


- 4 X = SO<sub>3</sub>K; Y = OH; Z = Me  
 5 Y + X = -(O-SO<sub>2</sub>)-; Z = Me  
 6 Y + X = -(O-SO<sub>2</sub>)<sub>2</sub>-; Z = Me  
 7 X = Y = Z = H

- 8 R = H  
 9 R = Me

after workup potassium 2-10-sulfonate as the only assigned product (entry 7a).

Scheme 1. Sulfonation of isopyrene (1) with SO<sub>3</sub>



Reaction of 5,10-dimethylisopyrene (3) with 2.0 mol-equiv. of SO<sub>3</sub> in dichloromethane as solvent affords after workup with water and subsequent neutralization with aqueous potassium hydroxide a compound of which the <sup>1</sup>H- and <sup>13</sup>C-NMR data are similar to those of 1,6:8,13-ethanediylidene[14]annulene (7)<sup>[32,33]</sup>, except for the two <sup>13</sup>C absorptions at  $\delta = 77.0$  and  $79.0$ . The latter absorptions are in the region reported for  $\beta$ -methoxy- and  $\beta$ -hydroxyalkane- $\alpha$ -sulfonates derived from alkenes by reaction with SO<sub>3</sub> and subsequent alkaline hydrolysis of the initially formed  $\beta$ -sul-

tones<sup>[34]</sup>. The product obtained eventually from 3 is therefore assigned to be potassium 16-hydroxy-7,14-dimethyl-1,6:8,13-ethanediylidene[14]annulene-15-sulfonate (4)<sup>[33]</sup>.

## Discussion

The only process that occurs on reaction of isopyrene (1) and 5-methylisopyrene (2) with the various SO<sub>3</sub> reagents employed in the present study is sulfodehydrogenation, the products being 1-5-S, 1-5,10-S<sub>2</sub> and 2-10-S. With the substrates 1 and 2, SO<sub>3</sub> behaves apparently as a monodentate electrophile with substitution at the most reactive position(s) of the 14 $\pi$  electron perimeter. However, if the(se) most reactive perimeter position(s) carry a methyl group, then the SO<sub>3</sub> could react as a bidentate electrophile with addition at the central C=C bond. In fact, sulfonation of 5,10-dimethylisopyrene (3) with 2.0 mol-equiv. of SO<sub>3</sub> in dichloromethane, followed by quenching with water and subsequent neutralization with aqueous potassium hydroxide, furnishes in high yield potassium 16-hydroxy-7,14-dimethyl-1,6:8,13-ethanediylidene[14]annulene-15-sulfonate (4) (Table 1, entry 7b). This observation is a strong indication for the initial formation of 7,14-dimethyl-1,6:8,13-ethanediylidene[14]annulene-15,16-sultone (5) and/or the corresponding pyrosultone 6 in the sulfonation reaction mixture. Apparently, SO<sub>3</sub> reacts as a bidentate electrophile with 3 in a reversible reaction<sup>[39]</sup> to give the  $\beta$ -sultone 5 (Scheme 2, steps 1 and -1) which may react with another molecule of SO<sub>3</sub> to give the corresponding pyrosultone 6 (step 2). Upon hydrolysis and subsequent neutralization the sultones 5 and 6 will then give the observed potassium 16-hydroxy-15-sulfonate 4 (steps 3 and 4).

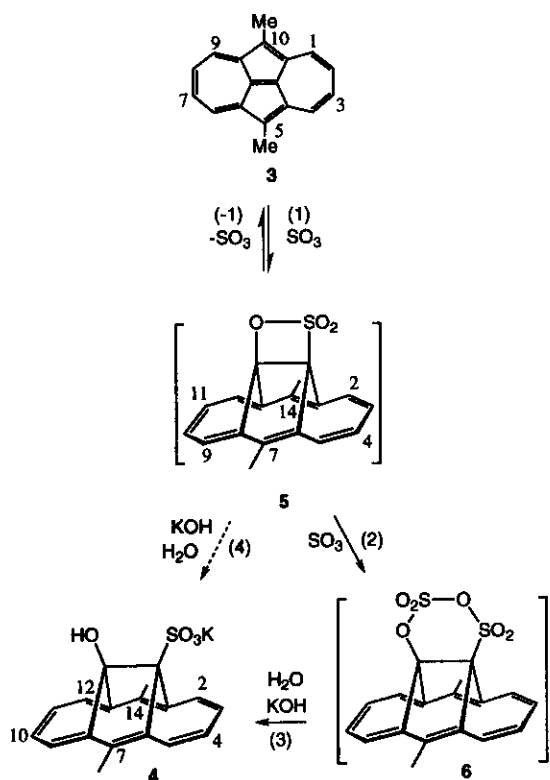
Isopyrene (1) may be considered as two fused azulene molecules. Monosulfonation of azulene (8) with SO<sub>3</sub> yields 8-1-S and further sulfonation gives quantitatively 8-1,3-S<sub>2</sub>. 1-Methylazulene (9) reacts with 3.0 mol-equiv. of SO<sub>3</sub> to yield quantitatively 9-3-S which is not further sulfonated<sup>[40]</sup>. The sulfonation behaviour of isopyrene (1) and its 5-methyl derivative 2 thus appears to be very similar to that of azulene (8) and its 1-methyl derivative 9 in that these compounds with SO<sub>3</sub> as reagent all undergo sulfodeprotonation

Table 2. <sup>1</sup>H-NMR data (solvent [D<sub>6</sub>]DMSO) of the isopyrenes 1–3 and their sulfonation products on reaction with SO<sub>3</sub> { $\delta$  value (multiplicity, J [Hz])}<sup>[a]</sup>

Compound	Hydrogen atom						
	1 (2)	2 (3)	3 (4)	4 (5)	5 (7)	6 (9)	7 (10)
1	9.00 (m)	8.41 (m)			8.35 (s)		
1-5-SO <sub>3</sub> K	9.00 (dd, 9)	8.40 (t)	8.45 (t)	9.56 (dd, 9)			8.32 (s)
1-5,10-(SO <sub>3</sub> K) <sub>2</sub>	9.57 (m)	8.42 (m)					
2	9.02 (m)	8.39 (m)	8.36 (m)	8.98 (m)	3.34 (s)		8.36 (s)
2-10-SO <sub>3</sub> K	9.51 (d, 10)	8.47 (t)	8.35 (t)	8.9	3.41 (s)		
3	8.93 (m)	8.30 (m)			3.34 (s)		
4 <sup>[a]</sup>	8.17 (m)	7.84 (m)			2.63 (s)	8.28 (m)	7.71 (m)

<sup>[a]</sup> The numbers in parentheses refer to the skeleton numbering of product 4 only.

Scheme 2. Mechanism of sulfonation of 5,10-dimethylisopyrene (3) with SO<sub>3</sub> in dichloromethane as solvent



exclusively in the five-membered ring at the carbon atom(s) adjacent to the seven-membered ring(s).

The authors wish to thank Prof. E. Vogel for stimulating the present investigation, and Dr. P. de Wit for performing some preliminary studies on the sulfonation of isopyrene.

### Experimental Section

The <sup>1</sup>H- and <sup>13</sup>C-NMR spectra were recorded with Bruker AC-200 and WM-250 spectrometers.

**Material:** Isopyrene (1) was synthesized starting from 9,10-dihydroanthracene<sup>18,41</sup>. 5,10-Dimethylisopyrene (3) was obtained by conversion of 1 with mercury(II) chloride into 5,10-bis(chloromercurio)isopyrene. Reaction of this bis(chloromercurio) derivative with *n*-butyllithium and subsequent methylation using methyl iod-

ide, afforded a mixture of 5-methyl- and 5,10-dimethylisopyrene (2 and 3) with a molar ratio of 19:81 in a combined isolated yield of 82%. The mixed product was used as such in experiment 7, listed in Table 1.

#### Sulfonation Procedures

**Method A:** To a heterogeneous mixture of 0.10 mmol of the substrate in 1.0 ml of nitromethane under argon was added at 25°C, while stirring, a solution of the desired amount of SO<sub>3</sub> contained in 1.0 ml of nitromethane. After 15 min of reaction at 25°C, the heterogeneous red reaction mixture was poured onto 5 ml of ice/water, the resulting solution neutralized with aqueous 1.0 M KOH, the solvents removed by bubbling nitrogen through the solution, and subsequent freeze-drying.

**Method B:** To a solution made up of 0.10 mmol of the substrate, 1.0 ml of dichloromethane and the required amount of dioxane (i.e. 1.1 mol-equiv. relative to the amount of SO<sub>3</sub>) was added at low temperature (-20 or -30°C) under argon the desired amount of SO<sub>3</sub>. After the chosen reaction time at -20 or -30°C, the heterogeneous dark-red reaction mixture was quenched and neutralized by slowly adding at ≤ -20°C, while vigorously stirring, an ice-cold solution of 0.2 ml of 1.0 M KOH in 2.0 ml of water. After allowing the temperature to rise to room temperature, the solvents were removed as described under method A.

**Method C:** To a solution, prepared at 17°C by slowly adding under argon, while stirring, 0.10 mmol of SO<sub>3</sub> to a solution of 0.11 mmol of dioxane in 0.5 ml of dichloromethane, was added at -20°C, while vigorously stirring, a solution of 0.05 mmol of the substrate in 0.5 ml of dichloromethane. After 4 h of stirring at -20°C, the heterogeneous red-brown reaction mixture was quenched with ice/water and worked up as described under method B.

**Method D:** To the heterogeneous sulfonating reagent, obtained at 17°C by the slow addition of 0.4 mmol of SO<sub>3</sub> under argon while stirring to 1.0 ml of dioxane, was added at the same temperature, under vigorous stirring, a solution containing 0.10 mmol of the substrate in 1.0 ml of dichloromethane. After 15 min of reaction at 17°C, the heterogeneous mixture was quenched and worked up as described under method A.

**Method E:** To a solution of 0.10 mmol of the substrate in 1.0 ml of [D<sub>2</sub>]dichloromethane (entry 6) or dichloromethane (entry 7) was added, under argon at -25°C while vigorously stirring, 0.20 mmol of SO<sub>3</sub>. After 15 min at -25°C, an <sup>1</sup>H-NMR spectrum of the reaction mixture in [D<sub>2</sub>]dichloromethane was recorded. Eventually - after 4.0 and 5.0 h, respectively - the heterogeneous reaction mixture was quenched and worked up as described under method B.

Table 3. <sup>13</sup>C-NMR data (solvent [D<sub>6</sub>]DMSO) of the isopyrenes 1-3 and their sulfonation products on reaction with SO<sub>3</sub> (δ values)<sup>[a]</sup>

Compound	Carbon atom												
	1 (2)	2 (3)	3 (4)	4 (5)	5 (7)	6 (9)	7 (10)	10 (14)	4a (6)	9a (13)	10b (15)	10c (16)	5-(7-)Me
1	129.21	130.82	-	-	114.91	-	-	-	143.26	-	123.05	-	-
1-5-SO <sub>3</sub> K	129.68	131.05	131.12	130.10	132.7	-	-	114.93	-	-	121.35	-	-
1-5,10-(SO <sub>3</sub> K) <sub>2</sub>	130.52	131.31	-	-	132.28	-	-	-	-	-	119.73	-	-
2	128.4	130.7 <sup>[b]</sup>	129.5 <sup>[b]</sup>	127.0	119.64	-	-	115.0	141.14	143.3	124.67	-	11.03
3	126.0	129.39	-	-	119.66	-	-	-	141.09	-	124.74	-	11.11
4	121.2	125.0	-	-	-	122.9	126.5	-	-	-	77.0	79.0	11.52

<sup>[a]</sup> See note <sup>[a]</sup> of Table 2. - <sup>[b]</sup> The assignments may be reversed.

**NMR Analysis:** The various solid residues obtained by methods A to E were dissolved in  $[D_6]DMSO$  or  $D_2O$  as appropriate, and the  $^1H$ - and  $^{13}C$ -NMR spectra recorded, applying APT (attached-proton technique), COSY<sup>[42]</sup>, NOE<sup>[43]</sup> and CH correlation<sup>[44]</sup> techniques, as appropriate. The structural assignments of the components of the reaction mixtures were made on basis of the observed  $^1H$ -NMR chemical shifts, absorption area ratios and coupling constants in combination with the  $^1H$ -NMR shielding parameters of the  $SO_3H$  and  $SO_3^-$  substituents<sup>[31]</sup>. The  $^1H$ - and  $^{13}C$ -NMR assignments are compiled in Tables 2 and 3. The product compositions of the various reaction mixtures were determined by multicomponent  $^1H$ -NMR analysis<sup>[31]</sup>.

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