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Alkylation of Alkenes: Ethylaluminum Sesquichloride-Mediated Hydro-Alkyl Additions with Alkyl Chloroformates and Di-*tert*-butylpyrocarbonate

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Abstract: A general method for the hydro-alkyl addition to the nonactivated C═C double bond of alkenes using alkyl chloroformates (primary, secondary), **12**, and di-*tert*-butylpyrocarbonate, **52**, mediated by ethylaluminum sesquichloride ($Et_3Al_2Cl_3$) has been developed. Reaction of **12** and **52**, respectively, with $Et_3Al_2Cl_3$ gives an alkyl cation which is added to the alkene; hydride transfer to the adduct carbenium ion or, if applicable, 1,2-H shift followed by hydride transfer from $Et_3Al_2Cl_3$ to the rearranged adduct carbenium ion gives the saturated addition product. The reaction has been applied to 1-alkenes, 2-methyl-1-alkenes, internal double bonds, and to three cyclic alkenes. Special interest has been focused on alkylations of unsaturated fatty compounds, such as oleic acid (**2**), which are important renewable feedstocks. 2-Methylalkanes, 3-methylalkanes, 2,4-dimethylalkanes, 2,3-dimethylalkanes, 2,2,4-trimethylalkanes, cyclohexylalkanes, and carboxylic acids and esters with the respective branched alkyl chain have been synthesized with good to moderate yields.

Introduction

The alkylation of alkenes is of considerable importance.[1] However, there are no methods for the direct alkylation of nonactivated C═C double bonds with alkyl residues, such as the isopropyl group. Thermal radical additions of alkanes are applicable to terminal double bonds only, not to internal double bonds.[2,3] Cationic additions are restricted to tertiary alkanes: for example, the formation of isooctane by the reaction of isobutene and isobutane in the presence of concentrated acids and superacids.[4] Friedel−Crafts alkylations of alkenes are rarely used in preparative organic synthesis to form new C−C bonds because they tend to give mixtures of products, including oligomers and polymers of alkenes and mostly not the desired mono alkylation products.[5] Alkylations of alkenes have been thoroughly investigated by Olah[6] and Mayr,[7−10] who, in particular, considered factors which would favor the formation of mono-alkylation products. It was stated that 1:1 addition products are formed if the alkyl halide reacts faster with the alkene than with the alkylation product; otherwise, higher addition products will be obtained.[7] The relative dissociation rates of the alkyl halide and the alkylation product induced by the Lewis acid should reflect their relative rates of addition to a common alkene.[7a] Thus, mono alkylation products with isopropyl halides were neither obtained in reactions with propene and isobutene[7b] nor in the corresponding reactions with butadiene and isoprene.[11] Exclusively, oligomers and polymers were formed. In contrast, the $AlCl_3$-induced condensation of *tert*-butyl chloride with propene afforded a mixture of isomeric heptyl chlorides in 70% yield.[12] The formation of isomers depends on the applied Lewis acid.[13] Mayr and Striepe found that the reaction of *tert*-butyl chloride and propene induced by $ZnCl_2 \cdot Et_2O$ gave exclusively the mono-alkylation product 2-chloro-4,4-dimethylpentane.[7b]

It is known that alkyl chloroformates are fragmented in the presence of $AlCl_3$, with formation of CO_2 and the corresponding carbenium ions.[14,15] Also, silver(I)-induced dechlorodecarboxylations were used to generate reactive carbocations from alkyl

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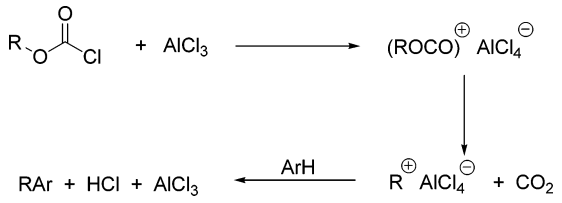
Scheme 1. Friedel−Crafts Alkylation of Arenes by $AlCl_3$-Induced Formation of Carbenium Ions from Chloroformates[14] [a]



[a] (Ar = Aryl, R = Alkyl)

chloroformates.[16] Previously Friedel and Crafts,[17] as well as Rennie,[18] showed that benzene is ethylated with ethyl chloroformate in the presence of $AlCl_3$ (Scheme 1).

Our special interest lies in the alkylation of long-chain unsaturated fatty compounds, such as oleic acid (**2**), since they are renewable raw materials of increasing significance[19−21] and alkyl-branched fatty compounds have interesting properties which make them attractive for use in cosmetic and lubricant applications.[22,23] Most of these characteristics, such as good spreadability, low viscosity, and good oxidative and hydrolytic stability, are shown by the commercially available product "isostearic acid" that is used in cosmetics and lubricants. However, this commercial isostearic acid that is formed as a byproduct in the montmorillonite-induced dimerization process of oleic acid is not at all a pure compound—it consists of a mixture of an immense number of components.[24] The synthesis of well-defined and completely characterized alkyl-branched fatty compounds by an addition reaction to, e.g., oleic acid, would be important.

We now report the results of our study, aimed to develop a general synthetic method for the hydro-alkylation of nonactivated C═C double bonds of alkenes with alkyl chloroformates mediated by ethylaluminum sesquichloride ($Et_3Al_2Cl_3$). Dichloromethane has been used as solvent without any nucleophilic properties. We performed a systematic investigation of the scope of the reaction with respect to alkenes (Figure 1) and to alkyl chloroformates (Figure 2) and could establish reaction conditions that allow the synthesis of the desired alkylation products in good to moderate yields.[25]

Results

First, we studied the hydro-alkyl addition to the 1,2-disubstituted C═C double bond of alkenes, such as *trans*-4-octene

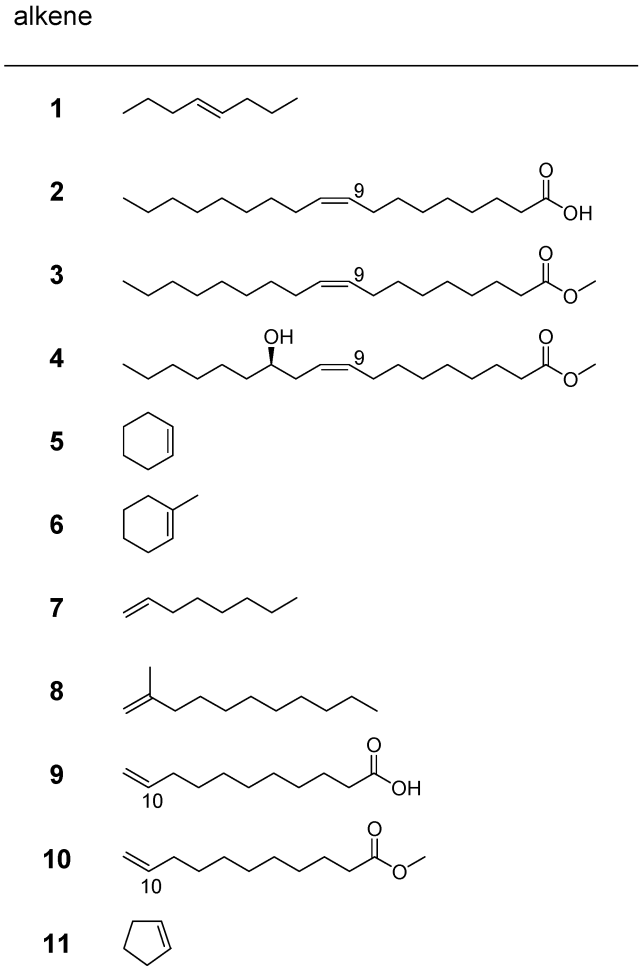
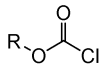


Figure 1. Alkenes **1**−**11** used in alkylation reactions.



12a-l

	R		R
a	isopropyl	**g**	1-hexyl
b	cyclohexyl	**h**	isobutyl
c	2-pentyl	**i**	neopentyl
d	1-propyl	**k**	ethyl
e	1-butyl	**l**	3-pentyl
f	1-pentyl		

Figure 2. Alkylation agents: alkyl chloroformates **12a**−**l**.

(**1**), oleic acid (**2**), methyl oleate (**3**), and methyl ricinoleate (**4**), and of cyclic alkenes, such as cyclohexene (**5**) and cyclopentene (**11**), using chloroformates of secondary alcohols, such as isopropyl (**12a**), cyclohexyl (**12b**), and 2-pentyl chloroformate (**12c**), as alkylating agents (Table 1). All products were unambiguously identified and characterized by ^1H NMR, ^{13}C NMR, GC/MS, and if applicable, by comparison with literature data.

Dropwise addition of ethylaluminum sesquichloride ($Et_3Al_2Cl_3$) to a mixture of alkene **1** and isopropyl chloroformate (**12a**)

(15) (a) Olah, G. A.; Olah, J. A. In *Carbonium Ions*; Olah, G. A., von R. Schleyer, P., Eds.; Wiley: New York, 1970; Vol. II, pp 715−782 (at p 765). (b) Kirmse, B. *Top Curr. Chem.* **1979**, *80*, 125−311 (at p 172).
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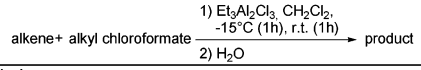
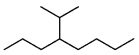
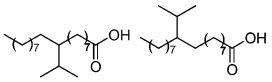
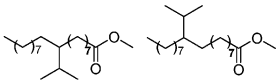
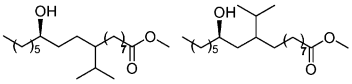
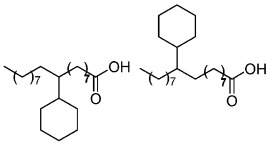
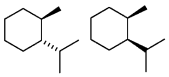
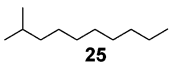
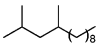
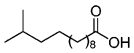
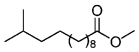
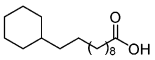
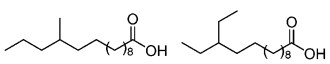
(23) Johnson, R. W., Jr.; Cantrell, R. R. In *Kirk Othmer Encyclopedia of Chemical Technology*, 4th ed.; New York: Wiley, 1993; Vol. 5, 189−192.
(24) Technical Data Sheet, Emersol 874 Isostearic Acid, Henkel Coorporation: Gulph Mills, PA, 1999.
(25) For a preliminary account of our results, see: Biermann, U.; Metzger, J. O. *Angew. Chem., Int. Ed.* **1999**, *38*, 3675−3677.

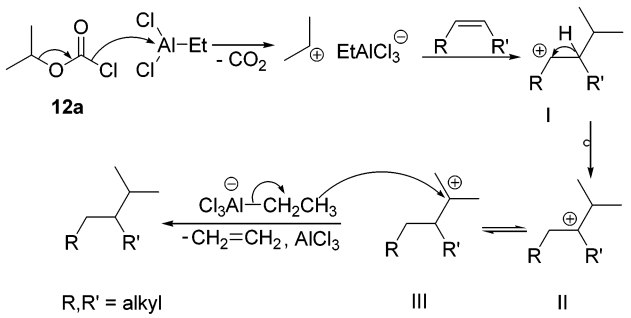
Table 1. Ethylaluminum Sesquichloride ($Et_3Al_2Cl_3$)-Induced Alkylations of Alkenes **1**−**11** with Secondary Alkyl Chloroformates: Isopropyl (**12a**), Cyclohexyl (**12b**), and 2-Pentyl Chloroformate (**12c**)



entry	alkene	alkyl chloroformate	product	ratio	yield [%][a]
1	**1**	**12a**	 **13**		67
2	**2**	**12a**	 **14** **15**	[**14**]:[**15**] ≈ 1:1	73
3	**3**	**12a**	 **16** **17**	[**16**]:[**17**] ≈ 1:1	71
4[b]	**4**	**12a**	 **18** **19**	[**18**]:[**19**] ≈ 1:1	60
5	**2**	**12b**	 **20** **21**	[**20**]:[**21**] ≈ 1:1	83
6[c]	**5**	**12a**	 **22**		82
7[c]	**11**	**12a**	 **23**		69
8	**6**	**12a**	 ***trans*-24** ***cis*-24**	[*trans*-**24**] :[*cis*-**24**] = 1.5:1	49
9[c]	**7**	**12a**	 **25**		55
10[c]	**8**	**12a**	 **26**		47
11[c]	**9**	**12a**	 **27**		60
12[c]	**10**	**12a**	 **28**		72
13[c]	**9**	**12b**	 **29**		58
14[c]	**9**	**12c**	 **30** **31**	[**30**]:[**31**] = 1.2:1	72

[a] Isolated yields were obtained by Kugelrohr distillation—except for products **14**/**15**, **20**/**21**, **27**, **29**, and **30**/**31** which were obtained by column chromatography (see Experimental Section). [b] The regioisomeric products **18** and **19** were obtained as mixtures of diasteromers, respectively, in ratios of 7:1 (**18**) and 5:3 (**19**). [c] The reaction was carried out with equimolar amounts of $Et_3Al_2Cl_3$ and triethylsilane.

Scheme 2. Mechanism of the Hydro-Alkylation of Internal Alkenes with Isopropyl Chloroformate (**12a**) and Ethylaluminum Sesquichloride



in dichloromethane in a ratio of 1:1:1 gave, after 1 h of reaction time at −15 °C and stirring for an additional 1 h at room temperature, the hydro-alkyl-addition product 4-isopropyloctane (**13**) in 67% yield (Table 1, entry 1). These are the standard reaction conditions that are used in the following experiments. It is important to use 1 equiv of $Et_3Al_2Cl_3$; 0.5 equiv is necessary for the chloro abstraction from the chloroformate, and 0.5 equiv is consumed in the hydride transfer to the adduct carbenium ion (see Scheme 2). Rearranged addition products and isomeric ethyl-isopropyloctanes were formed in small amounts, about 10% of the overall yield. Most reactions described in this paper showed comparable minor products (<10%) that will be outlined, furthermore, only in special examples. Chloro isopropyloctanes and isopropyloctenes were not detected, or were detected only in trace amounts, by GC/MS. The range of temperature that can be used to perform the reaction successfully is very small, thus preventing the investigation of the temperature dependence.

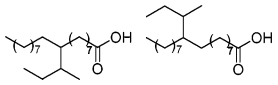
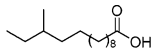
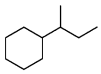
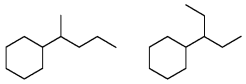
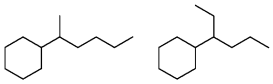
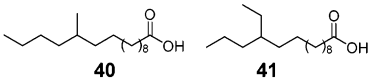
Alkylations of unsaturated fatty compounds **2** and **3**, containing two different alkyl substituents at the cis-configured double bond, afforded the regioisomeric mixtures of 9- and 10-isopropyloctadecanoic acid (**14** and **15**) and the respective methyl esters (**16** and **17**) in 73% and 71% yield, respectively (Table 1, entries 2 and 3). The regioisomers that could not be separated by chromatographic and other usual separation methods were obtained in a ratio of approximately 1:1. A respective mixture of the regioisomers 9- and 10-cyclohexyloctadecanoic acid (**20** and **21**) was formed on reaction of alkene **2** with cyclohexyl chloroformate (**12b**) (Table 1, entry 5). It seems to be remarkable that the yield is not diminished reacting substrates with carboxy and ester functionalities. In these reactions, it is important to apply 1.5 equiv of $Et_3Al_2Cl_3$ because 0.5 equiv is used by the carboxy group and the ester group, respectively. Also, an additional hydroxy group in the β-position relative to the C═C double bond is tolerated. The isopropylation of methyl ricinoleate (**4**) gave the alkylation products in 60% yield as a mixture of the two regioisomers **18** and **19** in a ratio of approximately 1:1. Both were formed as a pair of diastereomers; **18** in a ratio of 7:1 and **19** in a ratio of 5:3. The diastereomers were distinguishable by GC analysis and by the ^{13}C NMR spectrum, but they could not be assigned unambiguously to the respective compounds. In this example, 2 equiv of $Et_3Al_2Cl_3$ had to be applied because the reaction of the additional hydroxyl group with $Et_3Al_2Cl_3$ consumes 0.5 equiv (Table 1, entry 4).

The hydro-alkyl addition to cyclic alkenes, such as cyclohexene (**5**) and cyclopentene (**11**), with isopropyl chloroformate (**12a**) under the standard reaction conditions described for alkene **1** occurred with only moderate yields, e.g., 40%, of isopropylcyclohexane (**22**). Product mixtures, which consisted mainly of oligomers, were formed. However, the formation of the monoalkylation products could be favored by addition of a more effective hydride donor, such as triethylsilane.[10] Thus, the isopropylation of **5**, which was carried out by dropwise addition of an equimolar mixture of triethylsilane and Et_3AlCl_3 to the mixture of **5** and **12a**, afforded isopropylcyclohexane (**22**) in a remarkable yield of 82% (Table 1, entry 6).[25] The oligomerization was extensively suppressed using these modified standard reaction conditions. Isopropylcyclopentane (**23**) was synthezised in 69% yield using comparable reaction conditions (Table 1, entry 7). Remarkably, *cis*- and *trans*-1,2-dimethylcyclohexane were detected as minor products (together, 3.5%) by GC/MS. The reaction was also applied to the trialkyl-substituted C═C double bond of 1-methyl cyclohexene (**6**). The alkylation of **6** with **12a** was already complete after a reaction time of 1 h and gave *o*-menthane, **24**, in a yield of 49% as a diastereomeric mixture in a ratio of [*trans*-**24**]:[*cis*-**24**] = 1.5:1 (Table 1, entry 8). The isopropylation of 2-methyl-1-undecene (**8**), using standard reaction conditions, yielded only 10% of 2,4-dimethyltridecane (**26**). An additional product formed, in 45% yield, was 10,10,13-trimethyleicosane, the hydrodimer of **8**, as was shown by GC/MS. Addition of equimolar amounts of triethylsilane afforded a 47% yield of **26** but did not suppress the formation of the dimer completely (Table 1, entry 10). Most interesting was the hydro-isopropyl addition to 1-alkenes, giving selective access to 2-methylalkanes. The reaction of 1-octene (**7**), 10-undecenoic acid (**9**), and methyl 10-undecenoate (**10**) was studied. Under standard reaction conditions, the desired addition products were obtained in low yields only (e.g., reacting chloroformate **12a** with 10-undecenoic acid (**9**) produced hydroalkyl-addition product **27** in 10% yield, as determined by GC, because of dimerization and oligomerization of alkene **9**). By applying modified standard reaction conditions with addition of equimolar amounts of triethylsilane (alkene:**12a**:$Et_3Al_2Cl_3$:Et_3SiH = 1:1:1:1), oligomerization of the alkenes was considerably suppressed so that the mono-alkylation products **25, 27,** and **28** were isolated in yields of 55%, 60%, and 72%, respectively (Table 1, entries 9, 11, and 12).

The hydro-cyclohexyl addition to 1-alkenes opens an easy way to 1-cyclohexylalkanes. Reaction of 10-undecenoic acid (**9**) with cyclohexyl chloroformate (**12b**) in the presence of equimolar amounts of $Et_3Al_2Cl_3$ and triethylsilane afforded 11-cyclohexylundecanoic acid (**29**) in an isolated yield of 58% (Table 1, entry 13).

2-Pentyl chloroformate (**12c**) as a further secondary alkyl chloroformate was studied additionally because of a possible rearrangement of the intermediate 2-pentyl cation. As expected, in contrast to the respective reactions with chloroformates **12a** and **12b**, alkylation products obtained with **12c** were formed as mixtures of isomers. The alkylation of 10-undecenoic acid (**9**) yielded 72% of a mixture of 12-methylpentadecanoic acid (**30**) and 12-ethyltetradecanoic acid (**31**) in a ratio of 1.2:1 (Table 1, entry 14). 3-Pentyl chloroformate (**12l**) yielded the same ratio of the respective isomers in the corresponding reaction with cyclohexene (**5**) (Table 2, entry 6).

Table 2. Ethylaluminum Sesquichloride ($Et_3Al_2Cl_3$)-Induced Alkylations of Alkenes **2**, **5**, and **9** with Linear Primary Alkyl Chloroformates: 1-Propyl (**12d**), 1-Butyl (**12e**), 1-Pentyl (**12f**), and 1-Hexyl Chloroformate (**12g**)

entry	alkene	alkyl chloroformate	product	ratio	yield [%][a]
1	**2**	**12d**	**14/15**	[**14**]:[**15**] ≈ 1:1	71
2[b]	**9**	**12d**	**27**		56
3	**2**	**12e**	 **32** **33**	[**32**]:[**33**] ≈ 1:1	74
4[b]	**9**	**12e**	 **34**		72
5[b]	**5**	**12e**	 **35**		30
6[b,c]	**5**	**12f**	 **36** **37**	[**36**]:[**37**] = 1.3 : 1	28 (GC)
7[b]	**5**	**12g**	 **38** **39**	[**38**] : [**39**] = 1:1	37 (GC)
8[b]	**9**	**12g**	 **40** **41**	[**40**]:[**41**] = 1.1:1	44

[a] Isolated yields were obtained by column chromatography—except for product **35**, which was obtained by Kugelrohr distillation (see Experimental Section). [b] The reaction was carried out with equimolar amounts of $Et_3Al_2Cl_3$ and triethylsilane. [c] Using 3-pentyl chloroformate (**12l**), the ratio of [**36**]:[**37**] = 1.2:1 was obtained.

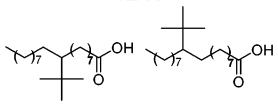
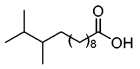
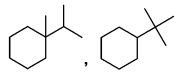
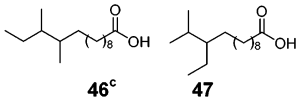
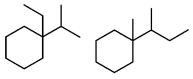
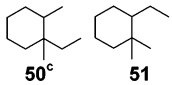
Having investigated the very general addition reactions of secondary alkyl chloroformates, we draw our attention to linear primary alkyl chloroformates. Reactions of ethyl chloroformate (**12k)** with 1-alkenes under standard reaction conditions, as well as with added triethylsilane, gave oligomerization of the alkene, e.g., the reaction of **9** and chloroformate **12k** resulted in the formation of a mixture of C_{22} dicarboxylic acids in 70% yield, as was shown by GC/MS. However, reacting 1-propyl chloroformate (**12d**) under standard reaction conditions with oleic acid (**2**) gave a mixture of 9- and 10-isopropyloctadecanoic acid (**14, 15**) in a yield of 71% (Table 2, entry 1). Thus, the same product mixture and almost the same yield were obtained as with isopropyl chloroformate (**12a**) (Table 1, entry 2). Analogously, reaction of chloroformate **12d** and 10-undecenoic acid (**9**) with added triethylsilane gave 12-methyltridecanoic acid (**27**) in 56% yield (Table 2, entry 2).

Using 1-butyl chloroformate (**12e**) in the reaction, the addition of the *sec*-butyl group could be expected. Indeed, reaction of oleic acid (**2**) under standard reaction conditions with chloroformate **12e** afforded the regioisomeric mixture of 9- and 10-*sec*-butyloctadecanoic acid (**32, 33**) in 74% yield. Analogously, reaction of alkene **9** with chloroformate **12e** in the presence of equimolar amounts of triethylsilane showed the addition of the 2-butyl cation, yielding 72% of 12-methyltetradecanoic acid (**34**). Cyclohexene (**5)** yielded only 30% of *sec*-butylcyclohexane (**35**). In addition, cyclohexylcyclohexane (36%, GC) was formed, the formation of which could not be suppressed by the addition of Et_3SiH.

Higher linear alkyl chloroformates are expected to give isomers by addition of the possible secondary alkyl groups which can be formed by Wagner−Meerwein rearrangements. Thus, alkylation of alkene **5** with chloroformate **12f** in the presence of triethylsilane yielded mixtures of 2- and 3-cyclohexylpentane in a ratio of [**36**]:[**37**] = 1.3:1. A product ratio of 1.2:1 was obtained using 3-pentyl chloroformate (**12l**) (Table 2, entry 6). A mixture of 12-methylhexadecanoic acid (**40**) and of 12-ethylpentadecanoic acid (**41**) in a ratio of [**40**]:[**41**] = 1.1:1 was obtained from the alkylation of alkene **9** with chloroformate **12g** in the presence of triethylsilane (Table 2, entry 8). Approximately the same ratio of products **38** and **39** was formed with alkene **5** (Table 2, entry 7).

It seems worth mentioning that, in all examples of reactions with primary alkyl chloroformates investigated, no hydro-1-alkyl-addition products could be detected. Primary alkyl chlo-

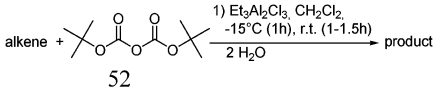
Table 3. Ethylaluminum Sesquichloride-Induced Alkylations of Alkenes **2**, **5**, **9**, and **11** with Branched Primary Alkyl Chloroformates: Isobutyl (**12h**) and Neopentyl Chloroformate (**12l**)

entry	alkene	alkyl chloro formate	product	ratio	yield [%][a]
1	**2**	**12h**	**32/33**  **42** **43**	**([32+33]):([42+43])** ≈ 2:1	74
2	**9**	**12h**	**34,**  **44**	**[34]**:**[44]** = 1:2.2	65
3[b]	**5**	**12h**	**35,**  **45** **54**	**[35]**:**[45]**:**[54]** = 12.5:2.5:1	41
4	**9**	**12i**	 **46**[c] **47**	**[46]**:**[47]** = 2.2:1	70
5	**5**	**12i**	 **48** **49**	**[48]**:**[49]** = 1.3:1	84
6	**11**	**12i**	 **50**[c] **51**	**[50]**:**[51]** = 2.8:1	65

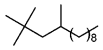
[a] Isolated yields were obtained by column chromatography (**32**/**33**/**42**/**43**, **34**/**44**, and **46**/**47**) or by Kugelrohr distillation (**35**/**45**/**54**, **48**/**49**, and **50**/**51**) (see Experimental Section). [b] The reaction was carried out with equimolar amounts of $Et_3Al_2Cl_3$ and triethylsilane. [c] 1:1 Mixture of diastereomers.

roformates that are branched at C-2 lead to the formation of interesting, rearranged addition products. We treated, therefore, oleic acid (**2**) with isobutyl chloroformate (**12h**) in the presence of $Et_3Al_2Cl_3$ and obtained a mixture of hydro-alkyl addition products **32, 33** and **42, 43** in 74% overall yield (Table 3, entry 1). Regioisomers **32** and **33** were also formed by reaction of **2** with 1-butyl chloroformate (**12e**) (Table 2, entry 3). Regioisomers **42** and **43** are the products of hydro-*tert*-butyl addition to the double bond and were also formed by reacting alkene **2** with di-*tert*-butylpyrocarbonate (**52**) (Table 4, entry 1). The ratio of ([**32**]+[**33**]):([**42**]+[**43**]**)** was approximately 2:1. Reaction of the same chloroformate, **12h**, with 1-alkene **9** showed a different outcome of products. Two isomeric addition products **34** and **44**, in a ratio of 1:2.2, were obtained. Whereas **34** was also obtained by addition of 1-butyl chloroformate (**12e**), no *tert*-butyl addition product was observed. Instead 11,12-dimethyltridecanoic acid (**44**) was formed (Table 3, entry 2), which was also obtained by reaction of **9** with di-*tert*-butylpyrocarbonate (**52**) (Table 4, entry 2). The respective reaction of cyclohexene (**5**) gave 2-butylcyclohexane (**35**), 1-isopropyl-1-methylcyclohexane (**45**), and *tert*-butylcyclohexane (**54**) in a ratio of 12.5:2.5:1. Product **35** was also formed in the reaction with chloroformate **12e (**Table 2, entry 5), and products **45** and **54**

Table 4. Ethylaluminum Sesquichloride-Induced Alkylations of Alkenes **2**, **5**, **8**, **9**, and **11** with Di-*tert*-butylpyrocarbonate (**52**)



52

entry	alkene	product	ratio	yield [%][a]
1	**2**	**42/43**	**[42]**:**[43]** ≈ 1:1	81
2[b]	**9**	**44**		60
3[b]	**8**	 **53**		43
4	**5**	**45,**  **54**	**[45]**:**[54]** = 4.7:1	71
5	**11**	 **55**		60

[a] Isolated yields were obtained by column chromatography (**42**/**43** and **44**) or by Kugelrohr distillation (**53**, **45**/**54**, and **55**) (see Experimental Section). [b] The reaction was carried out with equimolar amounts of $Et_3Al_2Cl_3$ and triethylsilane.

were obtained by reaction with di-*tert*-butylpyrocarbonate (**52**). (Table 3, entry 3; see also Table 4, entry 4).

It is remarkable that the alkylations of **9** and **5** with **12h** (Table 3, entries 2 and 3) showed only very small amounts of oligomerization products (>8%), although they were carried out under standard reaction conditions without addition of triethylsilane. In all examples described here, no trace of a hydro-isobutyl-addition product could be observed.

Next, neopentyl chloroformate (**12i**) was reacted with alkene **9**. 11,12-Dimethyltetradecanoic acid **(46**) and 11-ethyl-12-methyltridecanoic acid (**47)** were formed in a ratio of 2.2:1 and isolated in an overall yield of 70% (Table 3, entry 4). **46** was formed as a diastereomeric mixture in a ratio of about 1:1, as was shown by ^{13}C NMR. The respective reaction with cyclohexene (**5**) afforded 1-ethyl-1-isopropylcyclohexane (**48**) and 1-(2-butyl)-1-methylcyclohexane (**49**) in a ratio of 1.3:1 and an overall yield of 84% (Table 3, entry 5). Most interesting results were obtained reacting cyclopentene (**11**) with chloroformate **12i**. A mixture of 1-ethyl-1,2-dimethylcyclohexane (**50**) and 1-ethyl-2,2-dimethylcyclohexane (**51**) in a ratio of 2.8:1 and an overall yield of 65% were obtained. The two diastereomers of **50** were formed unselectively in a ratio of about 1:1, as was shown by ^{13}C NMR.

Finally, we were interested in the possibility of the addition of the *tert*-butyl group to nonactivated double bonds of alkenes. Because of its thermal instability, *tert*-butyl chloroformate could not be used, corresponding to **12a**−**l**, to study these reactions, so di-*tert*-butylpyrocarbonate (**52**) was applied to perform the reaction with alkenes **2**, **5**, and **9** (Table 4). To our complete satisfaction, pyrocarbonate **52** behaved as the chloroformates, **12**. The products obtained were already described for reactions with isobutyl chloroformate **12h**. Reaction of alkene **8** with pyrocarbonate **52** gave 2,2,4-trimethyltridecane (**53**), which could be isolated in 43% yield only (Table 4, entry 3). The dimerization of **8**, which resulted in the formation of about 18% of 10,10,12-trimethylicosane (GC), could not also be fully suppressed in the presence of Et_3SiH.

Finally, cyclopentene (**11**) was reacted with **52** (**11**:**52**:$Et_3Al_2Cl_3$ = 2:1:2). To our surprise, we isolated 1,1,2-trimethylcyclohexane (**55**) in 60% yield (Table 4, entry 5).

Discussion

The newly developed protocol of hydro-alkylation of alkenes is most important from a preparative point of view. Nonactivated C═C double bonds of alkenes have been hydro-alkylated using a very great variety of primary and secondary alkyl chloroformates, **12**, and di-*tert*-butylpyrocarbonate (**52**). Various functional groups in the substrate are tolerated. Thus, oleic acid (**2**), a renewable feedstock, was hydro-isopropylated to give a 1:1 mixture of 9- and 10-isopropylstearic acid (**14, 15**) (Table 1, entry 2)

The protocol allows for the highly efficient synthesis of 2-methylalkanes (isoalkanes) by reaction of 1-alkenes with isopropyl and 1-propyl chloroformate (Table 1, entries 9, 11, 12; Table 2, entry 2). ω-Unsaturated fatty acids give, most easily, (ω-1)-methyl-branched isofatty acids, an important class of natural compounds. Isofatty acids have been synthesized in a multistep procedure by Fordyce and Johanson.[26] 3-Methylalkanes are formed by reaction with 1-butyl chloroformate (Table 2, entry 4). 2,4-Dimethylalkanes may be obtained by reaction of 2-methyl-1-alkenes with isopropyl chloroformate (Table 1, entry 10), and 2,3-dimethylalkanes may be obtained by reaction of 1-alkenes with di-*tert*-butylpyrocarbonate (**52**) (Table 4, entry 2). Reacting 2-methyl-1-alkenes with **52** can provide 2,2,4-trimethylalkanes (Table 4, entry 3). Cyclohexylalkanes can generally be synthesized by reacting cyclohexyl chloroformate (**12b**) with alkenes (Table 1, entries 6 and 13). 11-Cyclohexylundecanoic acid (**29**) is known to be the main lipid of thermophilic archaebacteria.[27] The synthesis of the methyl ester of **29** has been performed by thermal radical addition of cyclohexane to the methyl ester of **9** (yield = 30%),[3] a method which is restricted to 1-alkenes for the synthesis of 1-cyclohexylalkanes.[2]

The main phenomena emerging from the results described in the preceding section, which should be posed for discussion, certainly are the differences in the substitution patterns of the addition products which may be influenced by the respective alkyl group of the chloroformate **12**, as well as by the alkene being reacted. Furthermore, an important phenomenon to be explained is the fact that the hydro-alkyl addition could be performed in many cases, e.g., with internal alkenes, under standard reaction conditions with the reagent ethylaluminum sesquichloride only, whereas in other examples, e.g., with 1-alkenes, the standard reaction conditions had to be modified by the addition of triethylsilane as an additional hydride donor to suppress the formation of oligomers. In contrast, when reacting alkenes **6** and **8**, the formation of dimers could only partially be suppressed by triethylsilane. The reaction mechanism should be able to explain these phenomena.

The basic reaction mechanism can be rationalized easily if alkylations were carried out with simple secondary alkyl chloroformates, such as isopropyl chloroformate (**12a**) (Scheme 2). In the presence of $Et_3Al_2Cl_3$, chloroformate **12a** decomposes by formation of CO_2 and the isopropyl cation, which adds to the C═C double bond of an internal alkene to give a secondary adduct carbenium ion I. One could have thought that hydride transfer to adduct carbenium ion I gives the hydro-alkyl-addition product. However, a 1,2-H shift affording the more stable tertiary carbenium ion II, possibly being in equilibrium with ion III, seems to be faster, as can be seen in the addition reactions of *tert*-butyl cation (see e.g., Scheme 7). Subsequent transfer of a hydride ion from an ethylaluminum species to the tertiary carbenium ions II and/or III and elimination of ethene lead to the hydro-alkyl addition product. It is known that ethylaluminum compounds can transfer hydride ions as well as ethyl groups;[28] notably, in this case, the hydride ion is transferred significantly more rapidly than the ethyl group, as is demonstrated by the small amount of ethylated products in most reactions. In addition, as shown in Scheme 3, chloride might be transferred as well to the carbenium ion to give alkyl-chloro-addition products,[7b] and a proton could be eliminated to give alkyl-dehydrogenation products.[29] The possible products of these two competitive reactions could not be observed and were formed—if at all—in very small amounts. Finally, the rearranged adduct carbenium ion could be trapped by the alkene to give

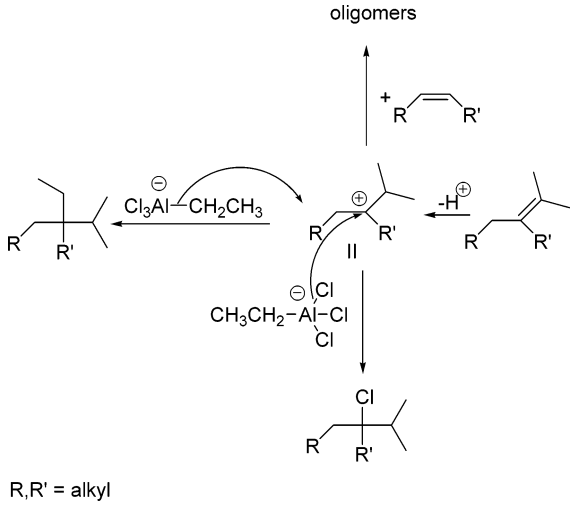
(26) Fordyce, C. R.; Johnson, J. R. *J. Am. Chem. Soc.* **1933**, *55*, 3368−3372.

(27) (a) Handa, S.; Floss. H. G. *Chem. Commun*. **1997**, 153−154. (b) Floss, H. G. *Nat. Prod. Rep.* **1997**, *14*, 433−452.

(28) Snider, B. B.; Rodini, D. J.; Karras, M.; Kirk, T. C.; Deutsch, E. A.; Cordova, R.; Price, R. T. *Tetrahedron* **1981**, *37*, 3927−3934.

(29) Snider, B. B.; Rodini, D. J.; Kirk, T. C.; Cordova, R. *J. Am. Soc*. **1982**, *104*, 555−563.

Scheme 3. Possible Competitive Reactions of the Hydro-Alkyl Addition Shown for the Rearranged Adduct Carbenium Ion II. Analogous Reactions Are Possible with Carbenium Ion III (Scheme 2)

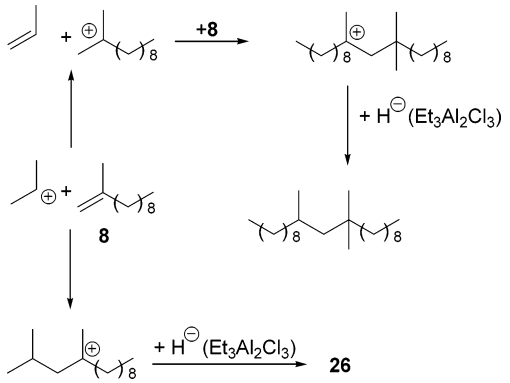


oligomers. This latter competitive reaction seems to be unimportant in reactions of internal alkenes because the most stable intermediate tertiary carbenium ion is sterically crowded and should be very unreactive in an addition to the internal alkene. In contrast, during reaction of 1-alkenes, the formed tertiary carbenium ion is less crowded, and addition to the 1-alkene will be as fast as or even faster than hydride transfer from the ethylaluminum species. Fortunately, reaction conditions could be found (adding Et_3SiH) such that hydride transfer to the adduct carbenium ion is the fastest trapping reaction which enables the hydro-alkyl-addition products to be obtained in 47−82% isolated yield (Table 1).

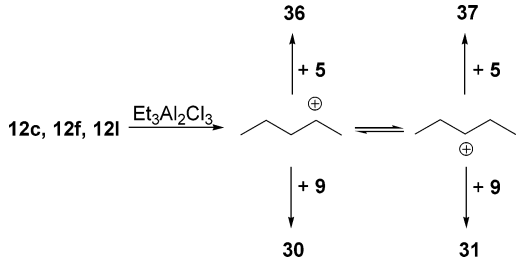
This basic reaction mechanism enables us to understand the results given in Table 1, entries 1−13. As can be expected, the primarily formed carbenium ion (isopropyl, cyclohexyl) is added without regioselectivity to oleic acid (**2**) and the respective methyl ester **3** (entries 2, 3, and 5). Unfortunately, the addition to methyl ricinoleate (**4**) occurs as well without regioselectivity (entry 4). Expectedly, high regioselectivity is observed in reactions of 1-alkenes (entries 9−13) and 1-methylcyclohexene (**6)** (entry 8). The lowest yields were obtained by reacting 2-methyl-1-undecene (**8**) because hydrodimers of **8** were formed in a competitive reaction which could not be fully suppressed by the addition of Et_3SiH. That is remarkable because, in the primary addition reaction, a stable tertiary cation is formed and direct hydride transfer to this adduct ion gives product **26** (Scheme 4). However, a stable tertiary cation is formed by β-hydrogen transfer from the isopropyl cation as well, and addition to alkene **8** followed by hydride transfer gives, finally, the hydrodimer. The same considerations apply to reactions of 1-methylcyclohexene (**6**). The minor yields of additions of butyl, pentyl, and hexyl cations may be explained by competitive β-hydrogen transfer from the secondary cations to cyclohexene (**5**) to give an internal alkene and a cyclohexyl cation that adds to cyclohexene, affording finally cylohexylcyclohexane (Table 2, entries 5−7).

It should be pointed out that the carbocations that are formulated for convenience as free carbocations in schemes 2−7 may exist as ion pairs stabilized by their anionic counterparts because dichloromethane is neither an ionizing nor a nucleophilic solvent. However, the carbocationic species formed are

Scheme 4. Mechanism of the Reaction of 2-Methyl-1-undecene (**8**) with the Isopropyl Cation Generated from Isopropyl Chlorformate (**12a**) in the Presence of $Et_3Al_2Cl_3$ (see Scheme 2) Giving Alkylation Product **26** and Hydrodimer 10,10,13-Trimethyleicosane



Scheme 5. Reaction of Pentyl Chloroformates **12f** and **12l** in the Presence of $Et_3Al_2Cl_3$ with Cyclohexene (**5**) and of **12c** with 10-Undecenoic Acid (**9**) Giving the Hydro-Alkylation Products **36**, **37** and **30**, **31**, Respectively



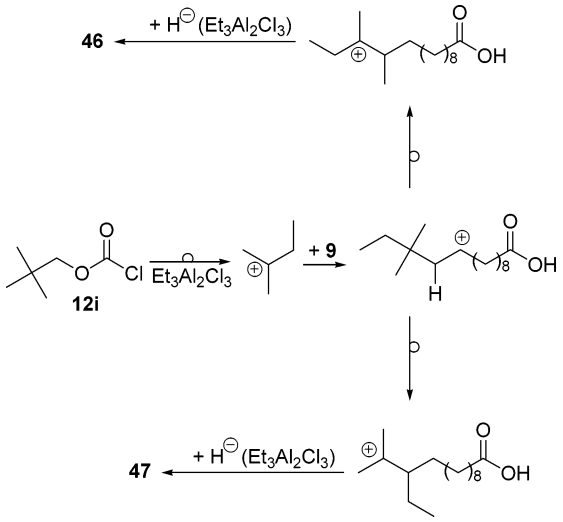
able to perform Wagner−Meerwein rearrangements,[30] being faster than the addition and the hydride transfer reaction. Thus, 2- (**12c**) and 3-pentyl chloroformate (**12l**) gave the same ratio of 2- and 3-addition products of 1.3:1, giving evidence that 3-pentyl cation is more stable than 2-pentyl cation (Scheme 5).

Reactions of primary alkyl chloroformates gave exclusively rearranged products with respect to the primary alkyl group (Tables 2 and 3). No primary addition products were observed in contrast to deaminations of 1-aminoalkanes which yielded rearranged and primary reaction products with water.[30] 1-Propyl chloroformate (**12d**) gave the same addition products and comparable yields as isopropyl chloroformate (**12a**). Obviously, during the $Et_3Al_2Cl_3$-mediated decomposition of **12d**, rearrangement of 1-propyl to isopropyl occurs, possibly by concerted 1,2-H shift and CO_2 elimination. The following reaction steps to give the final product occur as outlined in the basic reaction scheme (Scheme 2). The same applies to the reactions of chloroformates **12e**−**g** (Table 2, entries 3−8). The $Et_3Al_2Cl_3$-mediated decomposition of neopentyl chloroformate (**12i**) gives the *tert*-pentyl cation (Scheme 6), and the $Et_3Al_2Cl_3$-mediated decomposition of isobutyl chloroformate (**12h)** by two competitive 1,2-shifts of H and CH_3 gives *tert*-butyl and 2-butyl cation,[30] respectively, which are added to the respective alkene.

It can be assumed from the experimental results that the carbenium ions are fully equilibrated prior the addition to the alkene. Thus, reacting 2-pentyl chloroformate (**12c**) with alkene **9** (Table 1, entry 14) and 1-pentyl chloroformate (**12f**), as well as 3-pentyl chloroformate (**12l**) with cyclohexene(**5)** (Table 2,

(30) Keating, J. T.; Skell, P. S. In *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley: New York, 1970, Vol. II, pp 573−653.

Scheme 6. Mechanism of the Reaction of Neopentyl Chloroformate (**12i**) with Ethylaluminum Sesquichloride and 10-Undecenoic Acid (**9**) Giving Hydro-Alkylation Products **46** and **47**

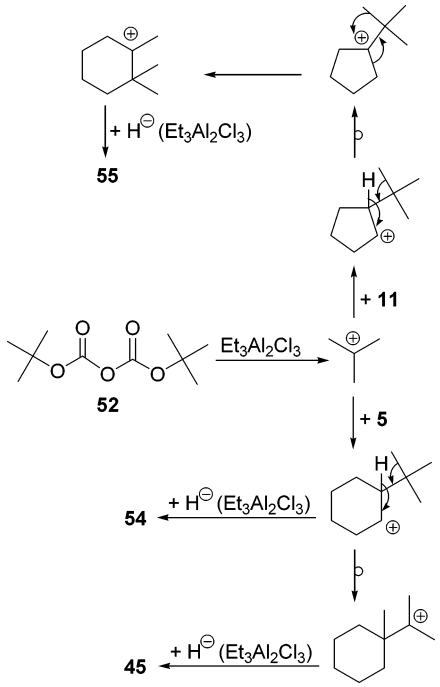


entry 6), gave the same ratio of 2- and 3-pentyl addition products (Scheme 5). The same applies to 1-hexyl chloroformate, **12g**, which was added to alkenes **5** and **9** to give the addition products in a ratio of 1:1 and 1.1:1, respectively (Table 2, entries 7−8). In comparison, deamination of 2-aminopentane in water gave 2- and 3-pentanol in a ratio of 3:1.[31]

Remarkably, a hydro-*tert*-butyl addition product was only observed by reacting alkenes with a 1,1-dialkyl-substituted double bond, such as in **8**, and with an internal double bond, such as in **2** and **5**, whereas 1-alkene **9** gives the rearranged product **44** (Table 3, entries 1−3; Table 4, entries 1−4). That can be straightforwardly rationalized. By addition of *tert*-butyl cation to alkene **8**, a stable tertiary adduct carbenium ion is formed, which is reacted with hydride to give product **53**. In contrast, by addition to 1-alkene **9**, a secondary adduct carbenium ion is obtained which can be stabilized by a 1,2-H shift and a following 1,2-CH_3 shift to give a tertiary carbenium ion. The following hydride transfer gives, highly selectively and preparatively very interestingly, a 2,3-dimethyl alkyl compound. Reacting alkenes containing an internal double bond, *tert*-butylated and rearranged products were observed. In the addition step, a secondary carbenium adduct ion is formed followed by 1,2-H shift to give a tertiary carbenium ion. Now, the product outcome seems to be controlled thermodynamically. In the case of alkene **2**, the *tert*-butylated products **42** and **43** are formed preferably. In contrast, in the case of cyclohexene (**5**), the exocyclic rearranged cation seems to be more stable,[32] and a ratio of [**45**]:[**54**] = 5:1 was observed (Scheme 7).

Addition of the *tert*-pentyl cation to alkene **9** occurs as outlined above for the *tert*-butyl cation addition. The difference is that methyl and ethyl can undergo 1,2-shifts competitively, giving two isomers (Scheme 6). The ratio of isomers **46** and **47** was found to be 2.2:1. Addition to cyclohexene (**5**) yielded analogously the addition products **48** and **49** (Table 3, entries 4, 5).

Scheme 7. Mechanism of Reactions of Di-*tert*-butylpyrocarbonate (**52**) in the Presence of $Et_3Al_2Cl_3$ with Cyclohexene (**5**) and Cyclopentene (**11**) To Give Alkylation Products **45**/**54** and **55**, Respectively



Addition reactions of *tert*-alkyl cations to cyclopentene (**11**) are most remarkable. Reaction with di-*tert*-butylpyrocarbonate (**52**) gave 1,1,2-trimethylcyclohexane (**55**) (Table 4, entry 5). No cyclopentane derivative could be detected. A rationalization of the formation of **55** is given in Scheme 7. Addition of the *tert*-butyl cation to **11** yields a secondary cyclopentyl cation. A 1,2-H shift followed by a concerted 1,2-CH_3 shift and a ring enlargement gives the most stable endocyclic *tert*-cyclohexyl cation and, finally, by hydride transfer, product **55.** Ring enlargement of 1-ethylcyclopentyl to 1-methylcyclohexyl cation[33] and of 2-(2-cyclopentyl)propyl cation to 1,2-dimethylcyclohexyl cation[34] is well known and studied by quantum mechanical calculations.[35] The respective addition of *tert*-pentyl cation by reaction with neopentyl chloroformate (**12i**) analogously gave the isomeric cyclohexane derivatives **50** and **51** because of a competitive 1,2-shift of methyl and ethyl in the adduct cation (Table 3, entry 6). Interestingly, reaction of isopropyl chloroformate (**12a**) with **11** yielded, as already discussed, isopropylcyclopentane as the major product (Table 1, entry 7). As minor products, *cis*- and *trans*-dimethylcyclohexane could be detected, formed clearly by ring enlargement as described above. These results show that the most stable product, carbenium ionic species, are formed, reacting finally with the hydride donor.

A few examples were studied giving diastereomeric products. Products **46** and **50** were formed unselectively; whereas the formation of products **18**/**19** and **24** showed low stereoselectivity, giving evidence that the reaction scheme may possibly be useful in stereoselective synthesis.

(31) Fry, J. L.; Karabatsos, J. J. In *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley: New York, 1970, Vol. II, pp 521−571.
(32) Siehl, H.-U.; Vrcek, V; Kronja, O. *J. Chem. Soc., Perkin Trans. 2* **2002**, 106−113.
(33) Lenoir, D.; Siehl, H.-U. In *Houben-Weyl*; Georg Thieme-Verlag: Stuttgart, 1990, Vol. E19c, p 264.
(34) Vrcek, V.; Siehl, H.-U.; Kronja, O. *J. Phys. Org. Chem.* **2000**, *13*, 616−6.

Conclusions

Our investigation of the ethylaluminum sesquichloride-mediated hydro-alkylation of a very broad variety of alkenes with alkyl chloroformates exhibiting different structural features clearly established the scope of this very general cationic hydroalkyl addition as a powerful synthetic tool. Some important classes of alkyl branched alkanes, e.g., 2-methylalkanes, 3-methylalkanes, 2,4-dimethylalkanes, 2,3-dimethylalkanes, 2,2,4-trimethylalkanes, and cyclohexylalkanes, can be generally synthesized with high to moderate yields. Important functional groups, e.g., carboxy, ester, and hydroxy, are compatible with the reaction conditions, enabling the selective synthesis of carboxylic acids, esters, and alcohols with a branched alkyl chain as given above for the respective alkanes.

Experimental Section

1. General Methods. All reactions were performed under nitrogen. Solvents were dried and distilled according to standard procedures.

Oleic acid and methyl oleate (new sunflower, 82.8% oleic acid, 3.6% stearic acid, 3.5% palmitic acid, 8.4% linoleic acid) and methyl ricinoleate (80−85% purity) were obtained from Cognis. The amounts of the starting olefins used in the reactions were calculated based on 100% purity. 10-Undecenoic acid and methyl 10-undecenoate were obtained from Atochem, and $Et_3Al_2Cl_3$ was obtained from Crompton GmbH. 1-Propyl, 1-hexyl, isobutyl, and neopentyl chloroformate, as well as 1-octene, *trans*-4-octene, cyclohexene, cyclopentene, and 2-methyl-1-undecene, were purchased from Aldrich and used as received. Isopropyl, cyclohexyl, and 1-butyl chloroformate were obtained from BASF, and 1-, 2-, and 3-pentyl chloroformate were synthezised as described.[36] For column chromatography Merck 60 silica gel, 70−230 mesh, was used. Analytical GC was performed on a Carlo Erba GC series 4160 with an FID detector and fused silica capillary column DB1, 29 m. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker AM 300 or Bruker AM 500 spectrometer at 20 °C using TMS (^{1}H NMR) and $CDCl_3$ (δ = 77.0 ppm, ^{13}C NMR) as internal standards. Selected data are given; full ^{1}H and ^{13}C NMR data are available from the authors on request. Mass spectra were recorded on a Finnigan MAT 212. All products were unambiguously identified by ^{1}H and ^{13}C NMR and by MS (EI) or GC/MS (EI). Refractive indices, n_D, were taken on a Zeiss-Abbé refractometer. Elemental analyses were performed by Mikroanalytisches Labor Beller, D-37004 Göttingen, Germany.

2. Synthesis of Alkylation Products. 2.1. Procedure 1 (Standard Reaction Conditions). A mixture of 5 mmol of the respective alkene and 5 mmol of the alkyl chloroformate, **12**, in CH_2Cl_2 (10 mL) was stirred in a N_2 atmosphere (1 bar) for 5 min at −15 °C. $Et_3Al_2Cl_3$ (1.24 g, 5 mmol for **1, 6**, and **9**−**11**; 1.86 g, 7.5 mmol for **2** and **3**, and 2.47 g, 10 mmol for **4**) was added dropwise over 1h (0.5 h for **6**) at −15 °C, and the solution was stirred at room temperature for an additional 1 h (0.5 h for **6**). Diethyl ether (100 mL), H_2O (40 mL), and 10% HCl, to dissolve precipitated aluminum salts, were then added. The organic phase was separated and washed with H_2O (3 × 30 mL). The combined extracts were dried over Na_2SO_4. The solvent was removed in vacuo.

Purification was achieved by Kugelrohr distillation or column chromatography, using petroleum ether/EtOAc (7:3) as eluent. Fractions containing the alkylation products were collected, the solvent was evaporated, and the residue was dried at 20 °C/0.01 mbar.

2.2. Procedure 2 (Modified Reaction Conditions with Addition of Triethylsilane). A mixture of 5 mmol of the respective alkene and of 5 mmol of the alkyl chloroformate, **12**, in CH_2Cl_2 (10 mL) was stirred in a N_2 atmosphere (1 bar) for 5 min at −15 °C. A mixture of triethylsilane (0.58 g, 5 mmol) and $Et_3Al_2Cl_3$ (1.24 g, 5 mmol) was then added dropwise over 1h at −15 °C, and the mixture was stirred for an additional 1 h at room temperature. Diethyl ether (100 mL), H_2O (40 mL), and 10% HCl, to dissolve precipitated aluminum salts, were then added. The organic phase was separated and washed with H_2O (3 × 30 mL). The combined extracts were dried over Na_2SO_4, the solvent was removed in vacuo, and the residues of experiments 8, 10 and 16 were dissolved in pentane and filtered through silica gel 60. After the pentane was evaporated, purification was achieved by Kugelrohr distillation. The residues of experiments 11, 12, 13, 15 and 17 were purified by column chromatography using petroleum ether/EtOAc (7:3). Fractions containing the alkylation product were collected, the solvent was evaporated, and the residue dried at 20 °C/0.01 mbar.

3. 4-Isopropyloctane (13). The reaction of *trans*-4-octene (**1**) (0.56 g, 5 mmol) and isopropyl chloroformate (**12a**) (0.7 g, 5 mmol) was carried out as described (procedure 1) and gave, after purification of the crude product by Kugelrohr distillation, 0.52 g (67%) of **13** as a colorless oil; n_D^{20} = 1.4239; ^{1}H NMR (300.1 MHz) δ = 0.88 (d, J = 6.9 Hz, 6H, CH_3), 0.94 (m, 6H, CH_3), 1.09 (m, 2H, CH_2), 1.32 (m, 8H, CH_2), 1.74 (m, 1H, 4-H); ^{13}C NMR (75.5 MHz) δ = 14.56 and 14.94 (C1 and C8), 19.52 and 19.56 ($CH(CH_3)_2$), 21.25 (C7), 23.35, 29.31 (C9), 30.45, 30.63, 33.32, 43.84 (C4); GC/MS (EI), *m*/z (%) 156(3), 112(66), 71(71), 57(100).

4. Mixture of 9-Isopropyloctadecanoic Acid (14) and 10-Isopropyloctadecanoic acid (15). The reaction of oleic acid (**2**) (1.41 g, 4.2 mmol) and isopropyl chloroformate (**12a**) or 1-propyl chlorformate (**12d**) (0.7 g, 5 mmol), respectively, was carried out as described (procedure 1) and gave, after purification of the crude product by column chromatography, 0.99 g (73%) and 0.97 g (71%), respectively, of a mixture of **14** and **15** (≈1:1) as a corlorless oil; n_D^{19} = 1.4588.

5. Mixture of Methyl 9-Isopropyloctadecanoate (16) and Methyl 10-Isopropyloctadecanoate (17). The reaction of methyl oleate (**3**) (1.48 g, 4.2 mmol) and isopropyl chloroformate (**12a**) (0.7 g, 5 mmol) was carried out as described (procedure 1) and gave, after purification of the crude product by Kugelrohr distillation, 1.02 g (71%) of a mixture of **16** and **17** (≈1:1) as a colorless oil; n_D^{20} = 1.4500; ^{1}H NMR (500.1 MHz) δ = 0.79 (d, J = 6.6 Hz, 6H, $CH(CH_3)_2$), 0.87 (t, J = 7.0 Hz, 3H, 18-H), 1.25 (m, 27 H, CH_2), 1.61 (m, 2H, 3-H), 1.66 (m, 1H, 9-H), 2.29 (t, J = 7.6, 2H, 2-H), 3.65 (s, 3H, OCH_3); ^{13}C NMR (125.8 MHz) δ = 14.07 (C18), 19.17 ($CH(CH_3)_2$), 22.66 (C17), 24.94 (C3), 31.91 $CH(CH_3)_2$), 34.10 (C2), 43.69 (C9(10)), 51.37 (OCH_3), 174.29 (C1); MS(EI), *m*/*z* (%) 340(10) [M$^+$], 309(2), 297(100), 265(25); $C_{22}H_{44}O_2$ (340.59) calcd, C 77.58, H 13.02; found, C 77.50, H 12.91.

6. Mixture of Methyl 12-Hydroxy-9-isopropyloctadecanoate (18) and Methyl 12-Hydroxy-10-isopropyloctadecanoate (19). The reaction of methyl ricinoleate (**4**) (1.56 g, 4.2 mmol) and isopropyl chloroformate (**12a**) (0.7 g, 5 mmol) was carried out as described (procedure 1) and gave, after purification of the crude product by Kugelrohr ditillation, 0.9 g (60%) of a mixture of **18** and **19**, which were formed as mixtures of diastereomers, respectively, in a ratio of 7:1 (GC) for **18** and 5:3 (GC) for **19,** as a colorless oil; n_D^{20} = 1.4605; ^{1}H NMR (500.1 MHz) δ = 0.82 (m, 9H, 18-H, $(CH_3)_2CH$), 1.23 (m, 22H, CH_2), 1.37 (m, 4H, 11-H, 13-H), 1.59 (m, 3H, 3-H, 9(10)-H), 2.27 (t, J = 7.5 Hz, 2H, 2-H), 3.55 (m, 1H, 12-H), 3.64 (s, 3H, OCH_3); ^{13}C NMR (125.8 MHz) δ = 14.02 (C18), 18.14 ($CHCH_3$), 19.05 ($CHCH_3$), 19.24 ($CHCH_3$), 22.57 (C17), 31.81 ($CH(CH_3)_2$), 34.05 (C2), 38.32 (C9(10)), 38.57 (C9(10)), 39.80 (C9(10)), 43.80 (C9(10)), 51.36 (OCH_3), 70.11 (C12), 70.41 (C12), 72.39 (C12), 72.44 (C12), 174.27 (C1); MS (CI, *iso*-butane) *m*/*z* (%) 357(18) [MH$^+$], 3.39(100) [MH$^+$ − H_2O]; HR-MS (EI) $C_{22}H_{44}O_3$ calcd, 356.3290; found, 356.3293.

7. Mixture of 9-Cyclohexyloctadecanoic Acid (20) and 10-Cyclohexyloctadecanoic Acid (21). The reaction of oleic acid (**2**) (1.41 g, 4.2 mmol) and cyclohexyl chloroformate (**12b**) (0.81 g, 5 mmol) was carried out as described (procedure 1) and gave, after purification of the crude product by column chromatography, 1.51 g (83%) of a mixture of **20** and **21** (≈1:1) as a pale yellow oil; n_D^{20} = 1.4712; ^{1}H

(35) Vrcek, V.; Saunders, M.; Kronja, O. *J. Org. Chem.* **2003**, *68*, 1859−1866.
(36) Petersen, S.; Piepenbrink, H.-F. In *Houben-Weyl*, 4th ed.; Georg Thieme-Verlag: Stuttgart, 1952; Vol. 8, 101−104.

NMR (500.1 MHz) δ = 0.89 (t, J = 7.1 Hz, 3H, 18-H), 0.95−1.35 (m, 32H, CH_2), 1.5−1.80 (m, 8H, 3-H, 9-H, CH-, and CH_2-*c*Hex), 2.35 (t, J = 7.7 Hz, 2H, 2-H), ^{13}C NMR (125.8 MHz) δ = 14.1 (C18), 34.0 (C2), 40.2 (CH-*c*Hex), 43.3 (C9(10)), 179.9 (C1); MS (EI) of the methyl esters of **20** and **21**, *m*/*z* (%) 380(15) [M^+], 349(3), 297(75), 264(22); HR-MS (EI) $C_{24}H_{46}O_2$ calcd, 366.3497; found, 366.3497.

8. Isopropylcyclopentane (23). The reaction of cyclopentene (**11**) (0.68 g, 10 mmol) and isopropyl chloroformate (**12a**) (1.4 g, 10 mmol) was carried out as described (procedure 2), using 2.48 g (10 mmol) of $Et_3Al_2Cl_3$ and 1.16 g (10 mmol) of Et_3SiH. After purification of the crude product by Kugelrohr distillation, 0.77 g (69%) of **23** was obtained**.** The product was characterized by GC/MS. As minor products, *cis*- (2%, GC) and *trans*-dimethylcyclohexan (2%, GC) were detected.

9. Synthesis of 1-Isopropyl-2-methyl-cyclohexane (24). The reaction of 1-methylcyclohexene (**6**) (0.48 g, 5 mmol) and isopropyl chloroformate (**12a**) (0.7 g, 5 mmol) was carried out as described (procedure 1) and gave, after purification of the crude product by Kugelrohr distillation, 0.44 g (49%) of **24** as a diastereomeric mixture ([*trans*-**24**]:[*cis*-**24**] = 1.5:1). *Trans*- and *cis*-**24** were characterized by their MS and NMR data; the latter are in agreement with the corresponding data given in ref 37.

10. 2,4-Dimethyltridecane (26). The reaction of 2-methylundecene (**8**) (0.84 g, 5 mmol) and isopropyl chloroformate (**12a**) (0.7 g, 5 mmol) was carried out as described (procedure 2) and gave, after purification of the crude product by Kugelrohr distillation, 0.5 g (47%) of **26**; ^{1}H NMR (300.1 MHz) δ = 0.93 (m, 12H, CH_3), 1.04 (m, 1H, 3-H_a), 1.18 (s, 16H, CH_2), 1.52 (m, 1H, 4-H), 1.71 (qqt, J = 6.8, 6.6, 6.6 Hz, 1H, 2-H); ^{13}C NMR (75.5 MHz) δ = 14.13 (C13), 19.85 (CH*C*H_3), 22.35 and 22.77 (CH(CH_3)$_2$), 23.48, 25.31, 27.09, 29.46, 29.76, 29.84, 30.13, 30.36, 32.02 (C2), 37.54 (C3), 46.97 (C4); $C_{15}H_{32}$ (212.42) calcd, C 84.80, H 15.18; found, C 84.90, H 15.20. In addition, 10,10,13-trimethyleicosane (29%, GC) was formed and identified by GC/MS (EI).

11. 12-Methyltridecanoic Acid (27). The reaction of 10-undecenoic acid (**9**) (0.92 g, 5 mmol) and isopropyl chlorformate (**12a**) or 1-propyl chloroformate (**12d**) (0.7 g, 5 mmol), respectively, was carried out as described (procedure 2) and gave, after purification of the crude product by column chromatography, 0.63 g (56%) and 0.68 g (60%) of **27**, respectively, as a solid; mp = 48−50 °C (ref 38, mp = 44−48 °C). The ^{1}H NMR spectrum and the mass spectrum (EI) of the methyl ester of **27** were in agreement with data given in refs 38 and 39.

12. 11-Cyclohexylundecanoic Acid (29). The reaction of 10-undecenoic acid (**9**) (0.92 g, 5 mmol) and cyclohexyl chloroformate (**12b**) (0.81 g, 5 mmol) was carried out as described (procedure 2) and gave, after purification of the crude product by column chromatography, 0.78 g (58%) of **29** as a solid; mp = 35−37 °C. The GC and MS data of the methyl ester of **29** were in agreement with those given in ref 3.

13. Mixture of 12-Methylpentadecanoic Acid (30) and 12-Ethyltetradecanoic Acid (31). The reaction of 10-undecenoic acid (**9**) (0.92 g, 5 mmol) and 2-pentyl chloroformate (**12c**) (0.75 g, 5 mmol) was carried out as described (procedure 2) and gave, after purification of the crude product by column chromatography, 0.92 g (72%) of a mixture of **30** and **31** ([**30**]:[**31**] = 1.2:1, GC) as a pale yellow oil; n_D^{20} = 1.4628; ^{1}H NMR (300.1 MHz) δ = 0.75−0.9 (m, 6H, 2× CH_3), 1.1−1.4 (m, 23H, CH_2, CH(**30**)), 1.50 (m, 1H, CH(**31**)), 1.63 (tt, J = 7.4, 7.2 Hz, 2H, 3-H), 2.34 (t, J = 7.2 Hz, 2H, 2-H); ^{13}C NMR (75.8 MHz) δ = 10.9 (CH_3, **31**), 14.1 (CH_3, C15), 19.6 (*C*H_3CH), 32.4 (C12, **30**), 34.3 (C2, **30** and **31**), 40.1 (C12, **31**), 180.4 (C1, **30** and **31**); GC/MS (EI) of the methyl esters of **30** and **31**; **30**, *m*/*z* (%) 270(15) [M^+], 227(15); **31**, *m*/*z* (%) 270(20) [M^+], 241(30); $C_{16}H_{32}O_2$ (256.43) calcd, C 74.92, H 12.58; found, C 75.07; H 12.21

14. Mixture of 9-*sec*-Butyloctadecanoic Acid (32) and 10-*sec*-Butyloctadecanoic Acid (33). The reaction of oleic acid (**2**) (1.42 g, 4.2 mmol) and 1-butyl chloroformate (**12e**) (0.69 g, 5 mmol) was carried out as described (procedure 1) and gave, after purification of the crude product by column chromatography, 1.06 g (74%) of a mixture of **32** and **33** (≈1:1) as a colorless oil; n_D^{20} = 1.4580; ^{1}H NMR (300.1 MHz) δ = 0.78 (d, J = 6.7 Hz, 3H, CH_3CH), 0.88 (2× t, J = 6.7 Hz, 6H, CH_3CH_2CH and 18-H), 1.15−1.45 (m, 30H), 1.63 (tt, J = 7.4, 7.1 Hz, 2H, 3-H), 2.35 (t, J = 7.5 Hz, 2H, 2-H); ^{13}C NMR (75.8 MHz) δ = 12.3 (CH_3CH_2CH), 14.0 (C18) 15.0 (*C*H_3CH), 34.0 (C2), 36.3 (CH_3*C*H), 42.0 (C9(10)), 180.0 (C1); MS (EI), *m*/*z* (%) 340(4) [M^+], 311(5), 283(100), 265(37); $C_{22}H_{44}O_2$ (340.59) calcd, C 77.58, H 13.02; found, C 77.52, H 12.98.

15. 12-Methyltetradecanoic Acid (34). The reaction of 10-undecenoic acid (**9**) (0.92 g, 5 mmol) and 1-butyl chloroformate (**12e**) (0.68 g, 5 mmol) was carried out as described (procedure 2) and gave, after purification of the crude product by column chromatography, 0.87 g (72%) of **34** as a colorless liquid; n_D^{20}= 1.4528; ^{13}C NMR (125.8 MHz) δ = 11.38 (C14), 19.20 (*C*H_3CH), 31.97 (C13), 34.13 (C12, C2), 36.64 (C11), 180.52 (C1); GC/MS (EI) of the methyl ester of **34**, *m*/*z* (%) 256(17) [M^+], 227(5), 225(5), 199(10), 74(100).

16. *sec*-Butylcyclohexane (35). The reaction of cyclohexene (**5**) (1.23 g, 15 mmol) and 1-butyl chloroformate (**12e**) (2.04 g, 15 mmol) was carried out as described (procedure 2), using 3.72 g (15 mmol) of $Et_3Al_2Cl_3$ and 1.74 g (15 mmol) of Et_3SiH. After purification of the crude product by fractionated micro distillation, 0.62 g (30%) of **35** was obtained**.** GC/MS (EI) of **35**, *m*/*z* (%) 140(27) [M^+], 111(37), 83-(100), 69(32). Additional cyclohexylcyclohexane (0.45 g, 40%) was formed. Mixtures of 2-pentylcyclohexane (**36)** and 3-pentylcyclohexane (**37**) in a ratio of [**36**]:[**37**] = 1.3:1 (GC), as well as 2-hexylcyclohexane (**38**) and 3-hexylcyclohexane (**39**) in a ratio of [**38**]:[**39**] = 1:1(GC), were obtained by analogous reactions with 1-pentyl chloroformate (**12f**), 3-pentyl chloroformate (**12l**), and 1-hexyl chloroformate (**12g**), respectively, and were characterized by GC and GC/MS.

17. Mixture of 12-Methylhexadecanoic Acid (40) and 12-Ethylpentadecanoic Acid (41). The reaction of 10-undecenoic acid (**9**) (0.92 g, 5 mmol) and 1-hexyl chloroformate (**12g**) (0.81 g, 5 mmol) was carried out as described (procedure 2) and gave, after purification of the crude product by column chromatography, 0.6 g (44%) of a mixture of **40** and **41** ([**40**]:[**41**] = 1.1:1, GC) as a colorless liquid; n_D^{20} = 1.4637; GC/MS (EI) of the methyl esters of **40** and **41** (the mass spectrum of the methyl ester of **40** was in agreement with the corresponding data given in ref 40); **41**, *m*/z (%) 284(40) [M^+], 253(5), 241(24), 199(50); $C_{17}H_{34}O_2$ (270.44) calcd, C 75.49, H 12.57; found, C 75.03, H 12.89.

18. Mixture of 12-Methyltetradecanoic Acid (34) and 11,12-Dimethyltridecanoic Acid (44). The reaction of 10-undecenoic acid (**9**) (0.92 g, 5 mmol) and isobutyl chloroformate (**12h**) (0.68 g, 5 mmol) was carried out as described (procedure 1) and gave, after purification of the crude product by column chromatography, 0.79 g (65%) of a mixture of **34** and **44** ([**34**]:[**44**] = 1:2.2, GC) as a colorless liquid; n_D^{20} = 1.4513.

19. Mixture of *sec*-Butylcyclohexane (35), 1-Methyl-1-isopropylcyclohexane (45), and *tert*-Butylcyclohexane (54). The reaction of cyclohexene (**5**) (0.82 g, 10 mmol) and isobutyl chloroformate (**12h**) (1.28 g, 10 mmol) was carried out as described (procedure 1), using 2.48 g (10 mmol) of $Et_3Al_2Cl_3$. After purification of the crude product by fractionated micro distillation, 0.58 g (41%) of a mixture of **35**, **45**, and **54** was obtained in a ratio of [**35**]:[**45**]:[**54**] = 12.5:2.5:1 (GC)**.** The mass spectra (EI) of **45** and **54** were in agreement with the published spectra (*NIST Chemistry Web Book*; NIST Standard Reference Database Number 69, March, 2003 Release; EPA MS numbers 158552 and 230537, respectively).

20. Mixture of 11,12-Dimethyltetradecanoic Acid (46) and 11-Ethyl-12-methyltridecanoic Acid (47). The reaction of 10-undecenoic

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acid (**9**) (0.92 g, 5 mmol) and neopentyl chloroformate (**12i**) (0.75 g, 5 mmol) was carried out as described (procedure 1) and gave, after purification of the crude product by column chromatography, 0.89 g (70%) of a mixture of **46** and **47** ([**46**]:[**47**] = 2.2:1, GC) as colorless liquid; $n_D^{20} = 1.4541$. **46** was formed as a diastereomeric mixture in a ratio of approximately 1:1(^{13}C NMR); GC/MS(EI) of the methyl esters of **46** and **47**; **46**, *m*/*z* (%) 270(39) [M$^+$], 255(1), 241(17), 239(8), 213(100), 181(36); **47**, *m*/*z* (%) 270(17) [M$^+$], 241(9), 239(3), 227(100), 195(23); $C_{16}H_{32}O_2$ (256.43) calcd, C 74.94, H 12.58; found, C 74.78, H 12.72.

21. Mixture of 1-Ethyl-1-isopropylcyclohexane (48) and 1-*sec*-Butyl-1-methylcyclohexane (49). The reaction of cyclohexene (**5**) (0.41 g, 5 mmol) and neopentylbutyl chloroformate (**12i**) (0.75 g, 5 mmol) was carried out as described (procedure 1) and gave, after purification of the crude product by Kugelrohr distillation, 0.65 g (84%) of a mixture of **48** and **49** ([**48**]:[**49**] = 1.3:1, GC)**.** GC/MS (EI) of **48** and **49**; **48**, *m*/*z* (%) 154(5) [M$^+$], 125(9), 111(100), 83(33), 69(77); **49**, *m*/*z* (%) 154(1) [M$^+$], 97(100), 69(8).

22. Mixture of 1-Ethyl-1,2-dimethylcyclohexane (50) and 1-Ethyl-2,2-dimethylcyclohexane (51). The reaction of cyclopentene (**11**) (0.34 g, 5 mmol) and neopentylbutyl chloroformate (**12i**) (0.75 g, 5 mmol) was carried out as described (procedure 1) and gave, after purification of the crude product by Kugelrohr distillation, 0.46 g (65%) of a mixture of **50** and **51** ([**50**]:[**51**] = 2.8:1 (GC)**.** Compound **50** was formed as a 1:1 mixture of diastereomers. GC/MS (EI) of **50** and **51**; **50**, *m*/*z* (%) 140(1) [M$^+$], 125(3), 111(100), 83(19), 69(87); **51**, *m*/*z* (%) 140(34) [M$^+$], 125(42), 111(12), 97(14), 83(22), 69(100).

23. Mixture of 9-*tert*-Butyloctadecanoic Acid (42) and 10-*tert*-Butyloctadecanoic Acid (43). A mixture of oleic acid (**2**) (0.72 g, 2.1 mmol) and di-*tert*-butylpyrocarbonate (**52**) (0.55 g, 2.5 mmol) in CH_2Cl_2 (10 mL) was stirred in a N_2 atmosphere (1 bar) for 10 min at −15 °C. $Et_3Al_2Cl_3$ (0.62 g, 2.5 mmol) was then added dropwise over 1 h at −15 °C, and the orange solution was stirred at room temperature for an additional 1 h. The reaction mixture was worked up as described (procedure 1). Purification of the regioisomeric mixture of **42** and **43 (1:1)** was achieved by treatment of the crude oil with urea[41] and gave 0.69 g (81%) as a pale yellow oil; $n_D^{20} = 1.4705$; ^{1}H NMR (300.1 MHz) 0.7−0.95 (m, 12H, 18-H, $(CH_3)_3$), 1.0−1.4 (m, 26H, CH_2), 1.62 (m, 3H, 3-H, 9-H), 2.43 (t, J = 7.5 Hz, 2H, 2-H); ^{13}C NMR (75.8 MHz) δ = 14.1 (C18), 24.4 $(CH_3)_3$), 39.5 ($C(CH_3)_3$), 40.6 (C9(10)), 179.8 (C1); MS(EI) was obtained from the methyl esters of **43/44**, *m*/*z* (%) 354(10) [M$^+$], 339(100); HR-MS (EI) $C_{22}H_{44}O_2$ calcd, 340.3341; found, 340.3337.

24. Synthesis of 11,12-Dimethyltridecanoic Acid (44). A mixture of 10-undecenoic acid (**9**) (0.92 g, 5 mmol) and di-*tert*-butylpyrocarbonate (**52**) (1,0 g, 5 mmol) in CH_2Cl_2 (10 mL) was stirred in a N_2 atmosphere (1 bar) for 10 min at −15 °C. A mixture of $Et_3Al_2Cl_3$ (1.48 g, 6 mmol) and Et_3SiH (0.58 g, 5 mmol) was then added dropwise over 1 h at −15 °C, and the mixture was stirred for an additional 1.5 h at room temperature. Further work up was carried out as described (procedure 2). Column chromatography (petroleum ether/EtOAc (7:3)) gave 0.72 g (60%) of **44** as a colorless oil; $n_D^{20} = 1.4605$; ^{13}C NMR (125.8 MHz) δ = 15.35 (CH_3CH), 17.97 (CH_3)$_2$CH), 20.25 (CH_3)$_2$-CH), 34.13 (C2 and C12), 34.40 (C10), 38.53 (C11), 180.52 (C1); GC/MS (EI) of the methyl ester of **44**, *m*/*z* (%) 256(37) [M$^+$], 241(2), 225(8), 213(86), 181(29), 74(100); $C_{15}H_{30}O_2$ (242.40) calcd, C 74.30, H 12.48; found, C 74.70, H 12.10.

25. 2,2,4-Trimethyltetradecane (53). A mixture of 2-methyl-1-undecene (**8**) (0.84 g, 5 mmol) and di-*tert*-butylpyrocarbonate (**52**) (0.77 g, 3.5 mmol) in CH_2Cl_2 (10 mL) was stirred in a N_2 atmosphere (1 bar) for 10 min at −15 °C. A mixture of $Et_3Al_2Cl_3$ (1.24 g, 5 mmol) and Et_3SiH (0.58 g, 5 mmol) was then added dropwise over 1 h at −15 °C, and the mixture was stirred for an additional 1 h at room temperature. Further work up was carried out as described (procedure 2). Kugelrohr distillation (70 °C, 8^{-3} mbar) gave 0.48 g (43%) of a colorless liquid, $n_D^{20} = 1.4349$; ^{1}H NMR (500.1 MHz) δ = 0.87 (m, 3H, 13-H), 0.88 (s, 9H, 1-H, $C(CH_3)_2$), 0.89 (m, 3H, $CH(CH_3)$), 1.01 (dd, J = 13.7, 6.3 Hz, 1H, 3-H), 1.21 (dd, J = 13.7, 3.4 Hz, 1H, 3-H′), 1.43 (m, 1H, 4-H), 1.30−1.21 (m, 16H, 5−12-H); ^{13}C NMR (125.8 MHz) δ = 14.1 (C1), 22.7 (C12, C14), 29.4−30.0 (C7−10), 30.0 (C1), 31.1 (C2), 34.0 (C4), 39.7 (C5), 51.4 (C3); HR-MS (EI) $C_{16}H_{34}$ calcd, 226.2660; found, 226.2660.

26. Mixture of 1-Isopropyl-1-methylcyclohexane (45) and *tert*-Butylcyclohexane (54). A mixture of cyclohexene (**5**) (0.41 g, 5 mmol) and di-*tert*-butylpyrocarbonate (**52**) (0.77 g, 3.5 mmol) in CH_2Cl_2 (10 mL) was stirred in a N_2 atmosphere (1 bar) for 10 min at −18 °C. $Et_3Al_2Cl_3$ (1.24 g, 5 mmol) was then added dropwise over 2 h at −18 °C, and the mixture was stirred for an additional 1 h at room temperature. Further work up was carried out as described (procedure 1). Kugelrohr distillation (120 °C, 1013 mbar) gave 0.50 g (71%) of a mixture of **45** and **54** in a ratio of [**45**]:[**54**] = 4.7:1 (GC) as a colorless liquid.

27. 1,1,2-Trimethylcyclohexane (55). A mixture of cyclopentene (**11**) (0.34 g, 5 mmol) and di-*tert*-butylpyrocarbonate (**52**) (0.55 g, 2.5 mmol) in CH_2Cl_2 (10 mL) was stirred in a N_2 atmosphere (1 bar) for 10 min at −18 °C. $Et_3Al_2Cl_3$ (1.24 g, 5 mmol) was then added dropwise over 2 h at −18 °C, and the mixture was stirred for an additional 1 h at room temperature. Further work up was carried out as described (procedure 1). Kugelrohr distillation (130 °C, 1013 mbar) gave 0.38 g (60%) of a colorless liquid. The mass spectrum (EI) of **55** was in agreement with the published spectrum (*NIST Chemistry Web Book*; NIST Standard Reference Database Number 69; March, 2003 Release; EPA MS number 114157).

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