Friedel–Crafts Alkylation of Alkenes: Ethylaluminum Sesquichloride Induced Alkylations with Alkyl Chloroformates**

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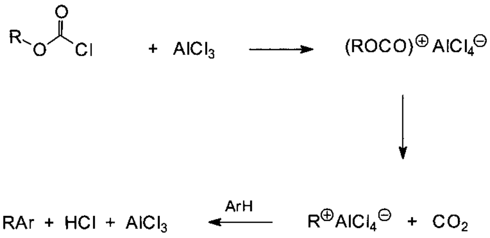
Dedicated to Professor Hansjörg Sinn
on the occasion of his 70th birthday

The alkylation of alkenes is of considerable importance.[1] Our interest lies in the alkylation of long-chain unsaturated fatty compounds such as oleic acid (**1a**) since they are renewable raw materials of increasing significance[2, 3] and alkyl-branched fatty compounds have interesting properties.[4] However, there are no methods for the direct alkylation of nonactivated C–C double bonds with simple alkyl residues such as the isopropyl group. Thermal radical addition of alkanes is applicable to terminal double bonds only, not to internal double bonds.[5] Friedel–Crafts alkylations of alkenes, which have been thoroughly investigated by Mayr et al., lead to 1:1 adducts only under certain restricted conditions.[6–9] Thus, $ZnCl_2$-induced reactions of isopropyl chloride with propene or isobutene gave no monoalkylation products, but exclusively oligomers.[6] Cationic additions of alkanes are restricted to tertiary alkanes, for example the formation of isooctane by the reaction of isobutene and isobutane in the presence of concentrated acids.[1, 10]

Friedel and Crafts[11] as well as Rennie[12] showed that benzene is ethylated with ethyl chloroformate in the presence of $AlCl_3$ (Scheme 1).[13] Chloroformates fragment in the presence of Lewis acids with the formation of carbenium



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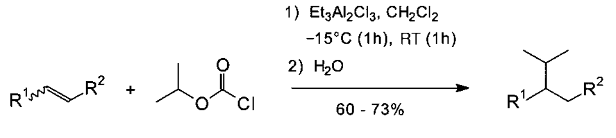
ions.[13, 14] We now report for the first time the alkylation of alkenes with alkyl chloroformates.

The reaction of oleic acid (**1a**) with isopropyl chloroformate (**2a**) in the presence of ethylaluminum sesquichloride ($Et_3Al_2Cl_3$) gave after 2 h a 1:1 regioisomeric mixture of 9- and 10-isopropyloctadecanoic acid (**3a**) in 73 % yield (Scheme 2). The analogous reaction with *trans*-4-octene (**1b**) gave 4-isopropyloctane (**3b**) in 67 % yield; small amounts (ca. 10 %) of the regioisomeric addition products and the regioisomeric ethylisopropyloctanes were also formed. In the reaction of methyl ricinoleate (**1c**) the alkylation product **3c** was obtained in 60 % yield as a mixture of regio- and diastereoisomers. Clearly the isopropyl cation formed from the chloroformate **2a** with $Et_3Al_2Cl_3$ adds to the C–C double bond of the alkenes **1a–c** and the subsequent transfer of a hydride ion from $Et_3Al_2Cl_3$ to the adduct carbenium ion leads to the saturated addition products **3a–c**. It is known that ethylaluminum compounds can transfer hydride ions as well as ethyl groups;[15] 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 product in all reactions.

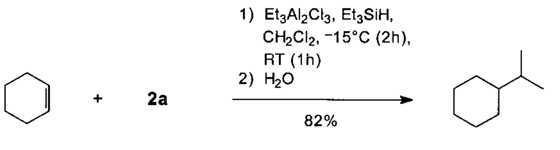


1a - c **2a** **3a - c**

1, 3	R^1	R^2
a	$(CH_2)_7CH_3$	$(CH_2)_7COOH$
b	$(CH_2)_3CH_3$	$(CH_2)_2CH_3$
c	$(CH_2)CHOH(CH_2)_5CH_3$	$(CH_2)_7COOCH_3$

Scheme 2. $Et_3Al_2Cl_3$-induced reaction of oleic acid (**1a**), *trans*-4-octene (**1b**), and methyl ricinoleate (**1c**) with isopropyl chloroformate (**2a**). Compound **3a** was obtained as a regioisomeric mixture (ca. 1:1), **3c** as a regioisomeric and diastereomeric mixture.

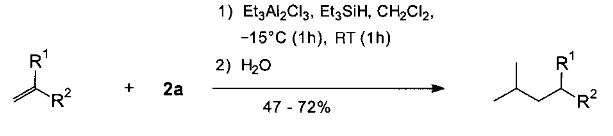
The alkylation of cyclic alkenes such as cyclohexene (**4**) under the reactions conditions described for the alkenes **1a–c** occurred with only moderate yields. A product mixture was formed which consisted mainly of oligomers. However, the addition of a more effective hydride donor, for example triethylsilane[9] considerably suppressed oligomerization, and isopropylcyclohexane (**5**) was isolated in 82 % yield (Scheme 3).



4 **5**

Scheme 3. Alkylation of cyclohexene (**4**) with isopropyl chloroformate (**2a**).

The reactions of 1,1-dialkylethenes, such as 2-methyl-1-undecene (**6a**), and 1-alkenes, such as 1-octene (**6b**) and methyl 10-undecenoate (**6c**), with **2a** also proceeded predominantly with oligomerization; alkylation products **7a–c** were not formed or only in poor yields. The addition of an equimolar amount of triethylsilane, on the other hand, gave **7a–c** in 47–72 % yield (Scheme 4).



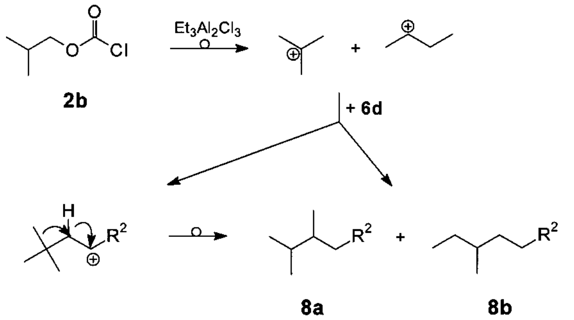
6a - c **7a - c**

6, 7	R^1	R^2
a	CH_3	$(CH_2)_8CH_3$
b	H	$(CH_2)_5CH_3$
c	H	$(CH_2)_8COOCH_3$
d	H	$(CH_2)_8COOH$

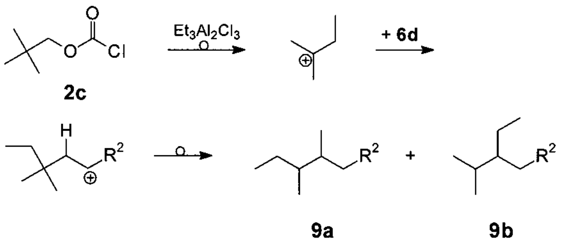
Scheme 4. Alkylation of 2-methyl-1-undecene (**6a**), 1-octene (**6b**), and methyl 10-undecenoate (**6c**) with isopropyl chloroformate (**2a**).

We have described a new method for the isopropylation of alkenes in which in an $Et_3Al_2Cl_3$-induced reaction an isopropyl cation is formed from the respective chloroformate and is added to the C–C double bond with subsequent hydride transfer. This addition can be applied to alkenes with a 1,2-dialkyl-substituted double bond and—with the addition of triethylsilane—also to 1-alkenes, 1,1-dialkylethenes, and cyclic alkenes. On the basis of these results the alkylation of alkenes should be possible with other alkyl chloroformates.

We have therefore treated 10-undecenoic acid (**6d**) in the presence of $Et_3Al_2Cl_3$ with the isobutyl (**2b**) and neopentyl (**2c**) esters of chloroformic acid, expecting interesting rearrangements. In both cases we obtained two constitutional isomeric addition products **8a/b** and **9a/b**, respectively, in a straightforward reaction (Schemes 5 and 6): after the rearrangement of the primary alkyl groups[16] and the addition, rearrangement of the carbenium ion adduct occurs. It is notable that as with the cationic addition of isobutane to 1-alkenes[10] no addition products with quaternary carbon atoms were found. Similar results were also



Scheme 5. Reaction of isobutyl chloroformate (**2b**) with 10-undecenoic acid (**6d**). The addition products **8a** and **8b** were formed in the ratio 2.2:1. $R^2 = (CH_2)_8COOH$.



Scheme 6. Reaction of neopentyl chloroformate (**2c**) with 10-undecenoic acid (**6d**). The addition products **9a** and **9b** were formed in the ratio 2.2:1. $R^2 = (CH_2)_8COOH$.

obtained with 2-ethylhexyl chloroformate. In contrast, reactions with ethyl chloroformate led to oligomeric products.

Experimental Section

General method for the synthesis of **3a–c**: A mixture of the respective alkene **1a** (1.42 g, 4.2 mmol), **1b** (0.56 g, 5 mmol), or **1c** (1.56 g, 4.2 mmol) and isopropyl chloroformate (**2a**) (0.7 g, 5 mmol) in CH_2Cl_2 (10 mL) was stirred in a N_2 atmosphere (1 bar) for 5 min at −15 °C. Then $Et_3Al_2Cl_3$ (1.86 g, 7.5 mmol for **1a**, 1.24 g, 5 mmol for **1b**, and 2.47 g, 10 mmol for **1c**) was added dropwise over 1 h at −15 °C and the solution was stirred at room temperature for a further 1 h. 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). After the combined extracts had been dried over Na_2SO_4 the solvent was removed in vacuum. Purification of **3a** was achieved by column chromatography (silica gel 60, 70–230 mesh, 1.7 × 33 cm) with petroleum ether/ethyl acetate (7/3, 300 mL) to yield 0.99 g **3a** (73%). Pure **3b** (0.52 g, 67%) and **3c** (0.90 g, 60%) were obtained by kugelrohr distillation.

General method for the synthesis of **5** and **7a–c**: A mixture of the respective alkene **4**, **6a–c** (5 mmol), and **2a** (0.7 g, 5 mmol) 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 1 h (2 h for **5**) at −15 °C and the mixture was stirred for a further 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). After the combined extracts had been dried over Na_2SO_4, the solvent was removed in vacuo, and the residues eluted over silica gel 60 with pentane. Evaporation of the pentane followed by kugelrohr distillation gave **5** (0.52 g, 82%), **7a** (0.50 g, 47%), **7b** (0.43 g, 55%), or **7c** (0.86 g, 72%).

General method for the synthesis of **8a/b** and **9a/b**: A mixture of **6d** (0.92 g, 5 mmol) and **2b** (0.68 g, 5 mmol) or **2c** (0.75 g, 5 mmol) in CH_2Cl_2 was stirred in a N_2 atmosphere (1 bar) for 5 min at −15 °C. Then $Et_3Al_2Cl_3$ (1.24 g, 5 mmol) was added as described for **3a–c**. The reaction mixtures were worked up as described and purified by column chromatography to give **8a/b**: (0.79 g, 65%) and **9a/b**: (0.89 g, 70%), respectively.

The products were identified by ^1H and ^{13}C NMR spectroscopy and mass spectrometry.

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