Some carbon, nitrogen- and carbon, oxygen-bond forming additions to unsaturated fatty compounds

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Unsaturated fatty compounds **1–7** were functionalized by ionic and free radical C,N- and C,O-bond forming additions to the C,C-double bond. C,N-bond forming additions of nitriles (*Ritter* reaction), iodine isocyanate, iodine azide, nitrogen oxides, nitrosyl chloride, N,N-dichlorourethane and azide as well as C,O-bond forming additions of alcohols and carboxylic acids are reviewed.

Einige Additionen an ungesättigte Fettstoffe unter Ausbildung von C,N- und C,O-Bindungen. Ungesättigte Fettstoffe **1–7** wurden durch ionische und radikalische Additionen an die C,C-Doppelbindung funktionalisiert. Über Additionen von Nitrilen (*Ritter*-Reaktion), Iodisocyanat, Iodazid, Stickoxiden, Nitrosylchlorid, N,N-Dichlorurethan und Azid unter Ausbildung einer C,N-Bindung und von Alkoholen und Carbonsäuren unter Ausbildung einer C,O-Bindung wird zusammenfassend berichtet.

1 Introduction

Unsaturated fatty acids such as 10-undecenoic acid (**1a**), oleic acid (**2a**), petroselinic acid (**3a**), erucic acid (**4a**), ricinoleic acid (**5a**), linoleic acid (**6a**), 5-eicosenoic acid (**7a**), and the respective esters, alcohols, and native oils (Fig. 1) are of considerable interest as renewable raw materials. These compounds are alkenes and contain an electron-rich double bond that can be functionalized in many different ways. It is therefore remarkable that over 90% of the reactions utilizing fatty acids have been focused on the carboxylic acid functionality [1].

In this review we would like to show how the C,C-double bond of fatty compounds can be converted by C,N- and C,O-bond forming addition reactions to give interesting functionalized fatty compounds.

2 Carbon, Nitrogen-Bond Forming Additions

2.1 Additions of nitriles (*Ritter* reaction)

Reactions of alkenes with nitriles in the presence of concentrated sulfuric acid, called *Ritter* reactions, give N-alkylamides after hydrolysis [2, 3]. The sulfuric acid induced *Ritter* reaction was applied to unsaturated fatty acids such as 10-undecenoic acid (**1a**), oleic acid (**2a**), and ricinoleic acid (**5a**) [4–8].

Reactions of **2a** with nitriles **8b–h** in 95% sulfuric acid afforded the corresponding substituted amidostearic acids **9b–h** as regioisomeric mixtures (Fig. 2) [4]. The crude products were obtained in yields of 89–99%, which show wide melting ranges (Tab. 1, Nr. 1–5). An isolated yield of the pure product was only given for acetamidostearic acid (**9b**), which was crystallized from acetone yielding 39% of pure product (Tab. 1, Nr. 1). The synthesis of **9b** could also be carried out by heating **2a** and **8b** (1:3) in a mixture of acetic acid and 70% perchloric acid (33:1) for 6 h at 90° C. Acrylamidostearic acid (**9c**) could not be induced to crystallize due to its high degree of isomerization (Nr. 2). Reactions with malonodinitrile (**8g**) and succinodinitrile (**8h**) afforded mixtures of the corresponding mono addition and bis addition products (Tab. 1; Nr. 6 and 7).

Reactions of oleic acid (**2a**) with the dinitriles of adipic, azelaic, and sebacic acid in concentrated sulfuric acid (2:1:12) are described by *Kulikova* et al. [6] to give exclusively the corresponding bisadducts in yields of 72–82%. Only the product from adipodinitrile could be crystallized from acetone (m.p. 73–80° C).

Additions of liquid hydrogen cyanide (**8a**) were carried out in 85–95% sulfuric acid to unsaturated fatty acids **1a, 2a** and **5a** [5]. The reactions afforded the corresponding formamido fatty acids **9a, 10** and **11** in yields of 80–97% as crude products (Tab. 2; Nr. 1–3). Pure products of **9a** and **10** were obtained after crystallization in yields of 21% and 16%, respectively. The amides **9a** and **10** could easily be hydrolyzed by refluxing with aqueous sulfuric acid for 5 h to give the corresponding free amino fatty acids after neutralization [5]. In contrast, hydrolysis of **9b** (Tab. 1; Nr. 1) proved to be difficult and needed 84 h to be nearly quantitative (94%) [4].

The addition of benzonitrile to methyl 10-undecenoate (**1b**) is described to give after saponification benzamidoundecanoic acid in a yield of 16% [8]. The position of the benzoylamino group on the molecule chain was not given.

The results of additions of acetonitrile (**8b**) and acrylonitrile (**8c**) to methyl esters of unsaturated fatty acids **1b–4b** in the presence of the Lewis acid tin tetrachloride are given in

Tab. 1. Substituted amidostearic acids by addition of nitriles **8b–h** to oleic acid (**2a**)[a] [4].

Nr.	Nitrile	Product	Yield[b] [%]	Melting range [°C]
1	**8b**	**9b**	39(99)	70–82
2	**8c**	**9c**	(89)	c)
3	**8d**	**9d**	(94)	64–75
4	**8e**	**9e**	(97)	87–90
5	**8f**	**9f**	(91)	69–78
6	**8g**	**9g**	d)	65–72
7	**8h**	**9h**	e)	117–118

[a] Typical reaction conditions: **2a**:**8**:H_2SO_4 (95%) = 1:3:6, 27–30° C, 15 min – 1 h.

[b] Yields of pure products; yields of crude products are given in brackets.

[c] Viscous liquid, which could not be induced to crystallize.

[d] Probably a regioisomeric mixture of cyanoacetamidostearic acid and malonamido-bis-stearic acid.

[e] Probably a mixture of β-cyanopropionamidostearic acid and succinamido-bis-stearic acid.

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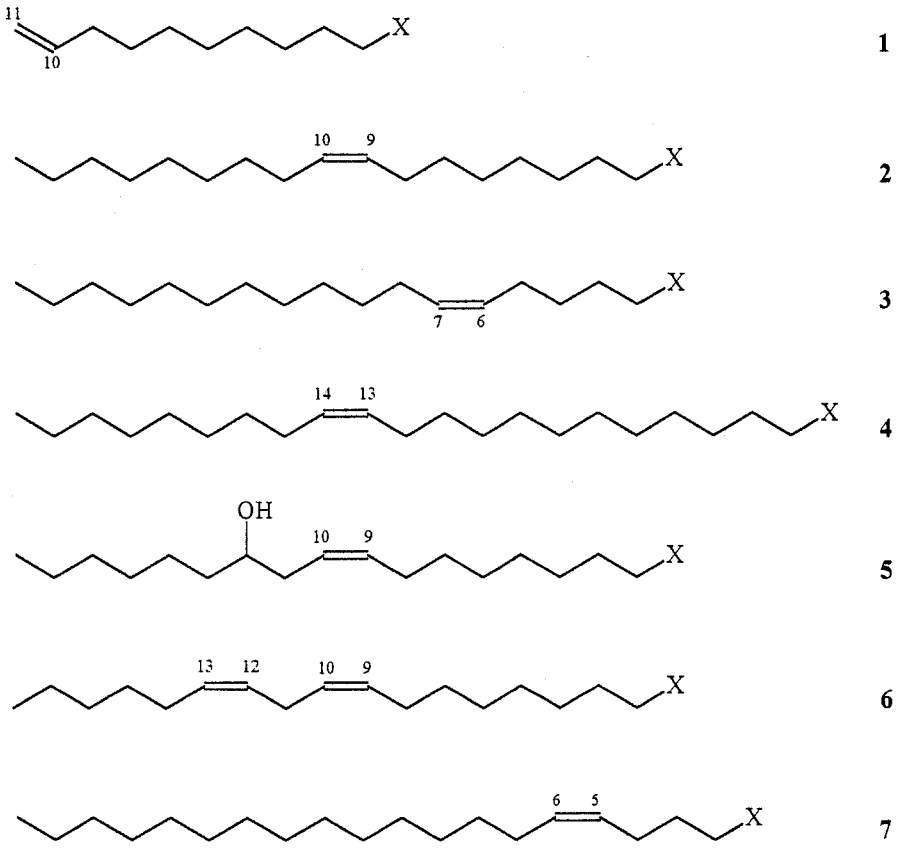
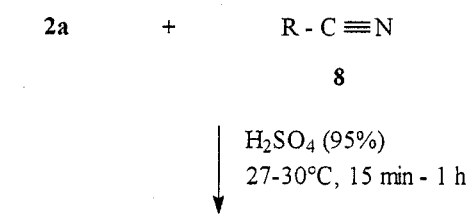
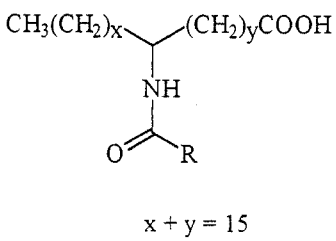


1-7	a	b	c
X	COOH	$COOCH_3$	CH_2OH

Fig. 1. Unsaturated fatty compounds **1–7**.





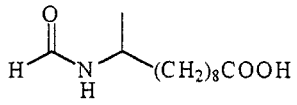
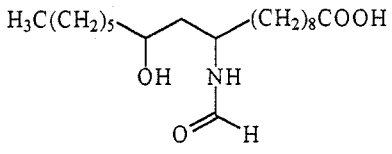
9a - h

x + y = 15

8, 9	a	b	c	d	e	f	g	h
R	H	CH_3	CH_2=CH	CH_3CH_2	C_6H_5	$HOOCCH_2$	$NCCH_2$	$NCCH_2CH_2$

Fig. 2. Addition of nitriles **8** to oleic acid (**2a**) in the presence of H_2SO_4.

Tab. 2. Addition of hydrogen cyanide (**8a**) to unsaturated fatty acids: preparation of formamido fatty acids[a] [5].

Nr.	Alkene	Product[b]	Yield[c] [%]	Melting range [°C]
1	**2a**	**9a**	21(96–97)	42–43
2	**1a**	 **10**	16(80)	91–93
3	**5a**	 **11**	– (84)	–

[a] Reaction conditions: alkene:**8a**:H_2SO_4 (85%) = 1:3:6, 20–30° C, 2 h.
[b] Products were obtained as isomeric mixtures.
[c] Yields of pure products; yields of crude products are given in brackets.

Tab. 3 [9, 10]. The reaction of e.g. nitrile **8c** and methyl 10-undecenoate (**1b**) induced by stoichiometric amounts of tin tetrachloride gave methyl acetamidoundecanoate (**12**, Fig. 3). The $SnCl_4$-induced addition of **8b** and **8c** was furthermore applied to unsaturated fatty esters such as **2b, 3b** and **4b** and afforded the corresponding substituted methyl alkylamido alkanoates **12–19** in good yields (crude products: 86–98%; 61–91% after crystallization). In contrast to sulfuric acid induced reactions the additions in the presence of $SnCl_4$ showed only moderate, temperature dependent isomerization. Addition product **15** e.g. was obtained after crystallization in 85% yield with a narrow melting range of 67–69° C (Tab. 3; Nr. 4). Mass spectrometric analysis revealed that 70% of product **15** was methyl 9- and 10-acrylamidostearate containing some percent of the 7-, 8-, 11- and 12-isomers. At a reaction temperature of 0° C no isomerization products were formed. Furthermore, the $SnCl_4$-induced addition of acrylonitrile (**8c**) was carried out with native oils, such as oleic acid rich rapeseed oil. The corresponding highly functionalized triglyceride was obtained after a reaction time of 48 h in a yield of 70% [11]. The addition products **13, 14, 16** and **18** were saponified by refluxing with 50% aqueous sulfuric acid as described by *Roe* and *Swern* [5] to give the corresponding free amino compounds in 35 to 50% yield [11].

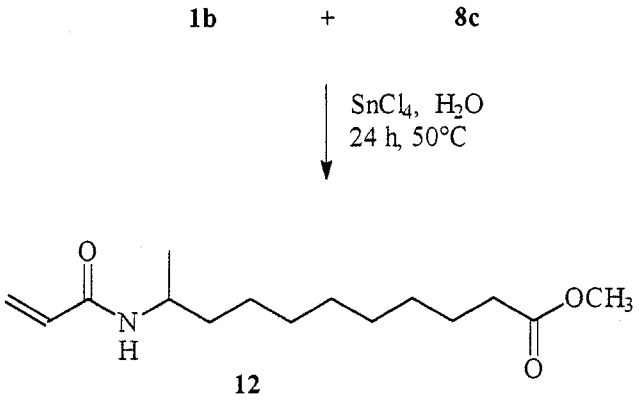


Fig. 3. $SnCl_4$-induced addition of acrylonitrile (**8c**) to methyl 10-undecenoate (**1b**).

2.2 Electrophilic additions of iodine isocyanate and iodine azide

Ansari and *Osman* [12] added iodine isocyanate, generated *in situ*, to methyl oleate (**2b**) (Fig. 4). The general procedure consists of reacting methyl oleate (**2b**) with silver cyanate and iodine in dry tetrahydrofurane at – 30° C. The resulting product was characterized as methyl *threo*-9(10)-iodo-10(9)-isocyanatooctadecanoate (**20**). The addition of iodine isocyanate proceeded in *anti* manner and led via a cyclic iodonium ion intermediate stereospecifically to the corresponding *threo*-β-iodoisocyanate. The further reaction of the β-iodoisocyanato derivative **20** by refluxing with anhydrous methanol led to the corresponding β-iodocarbamate **20a**. *Gebelein, Swift,* and *Swern* [13] generated in the same manner the β-iodocarbamate **21a** from oleyl alcohol **2c**. The products were obtained as oils in good yields (Tab. 4, Nr. 1–3). The β-iodocarbamates are important precursors for the synthesis of 2-oxazolidines [14] as well as for aziridines [15]. Addition of iodine isocyanate to methyl linoleate (**6b**) gave the mono addition product only. Addition of a second equivalent of iodine isocyanate was not possible [12].

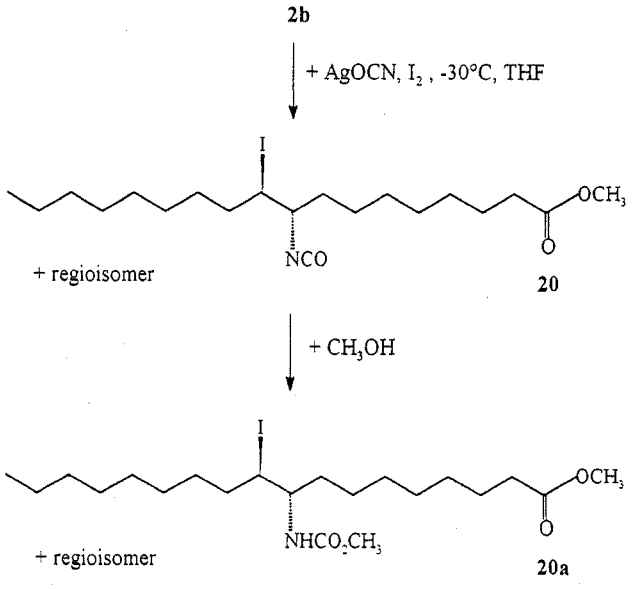
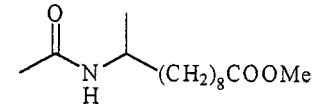
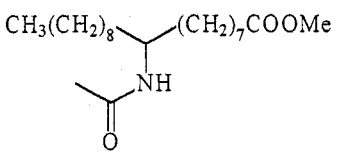
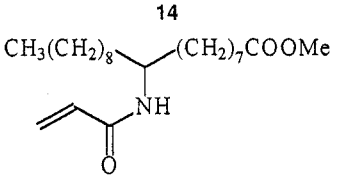
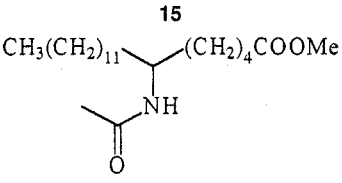
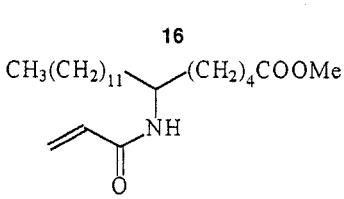
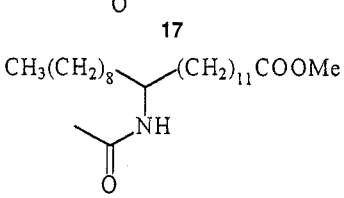
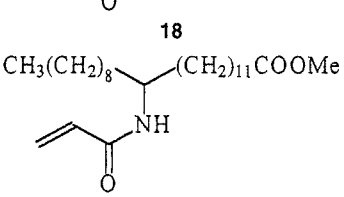
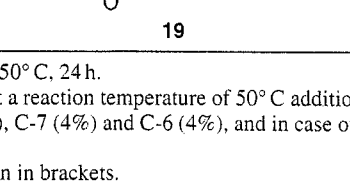


Fig. 4. Addition of iodine isocyanate to methyl oleate (**2b**) [12].

Tab. 3. $SnCl_4$-induced additions of acetonitrile (**8b**) and acrylonitrile (**8c**) to methyl esters of unsaturated fatty acids[a] [9, 10].

Nr.	Alkene	Nitrile	Product[b]	Yield[c] [%]	Melting range [°C]
1	**1b**	**8c**	**12** 	86 (92)	71–74
2	**1b**	**8b**	**13** 	89 (95)	54–56
3	**2b**	**8b**	**14** 	91 (98)	74–75
4	**2b**	**8c**	**15** 	85 (96)	67–69
5	**3b**	**8b**	**16** 	69 (98)	71–78
6	**3b**	**8c**	**17** 	61 (86)	66–67
7	**4b**	**8b**	**18** 	87 (93)	69–75
8	**4b**	**8c**	**19** 	83 (97)	64–66

[a] Reaction conditions: alkene:nitrile:$SnCl_4$:H_2O = 1:2:1:1, 50° C, 24 h.

[b] The products were obtained as regioisomeric mixtures. At a reaction temperature of 50° C additions of the nitriles occurred in case of **12** and **13** with regioselectivity to C-10 (47%), C-9 (31%), C-8 (7%), C-7 (4%) and C-6 (4%), and in case of **14–19** with 70–80% regioselectivity in equal amounts to both C-atoms of the respective double bond.

[c] Yields of pure products; yields of crude products are given in brackets.

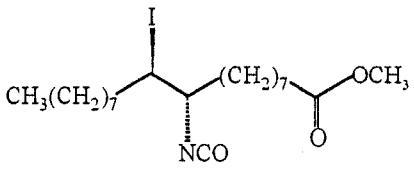
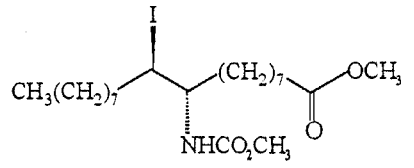
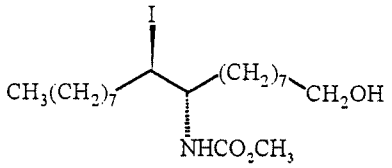
[d] Melting points were obtained after crystallization from methanol/water = 5:2.

Ali et al. [16] investigated the addition of iodine azide to methyl 10-undecenoate (**1b**) (Fig. 5) and methyl oleate (**2b**). The iodine azide was generated by adding iodine monochloride to a stirred slurry of sodium azide in acetonitrile at 0° C. The corresponding products methyl 10-azido-11-iodoundecanoate (**22**) and methyl *threo*-9(10)-azido-10(9)-iodooctadecanoate (**23**) were obtained in quantitative yields (Tab. 5, Nr. 1, 2).

2.3 Additions of nitrogen oxides N_2O_3, NO_2 and nitrosyl chloride

Kobayashi [17] investigated the free radical addition of NO_2 to the double bond of oleic acid (**2a**) (Fig. 6). By varying the reaction conditions (temperature, solvent, reaction time, and flow rate of NO_2) a mixture of 24% of 9,10-dinitrooctadecanoic acid (**24**) and 43% of 9(10)-nitro-10(9)-nitritooctadecanoic acid (**25**) and other minor products were

Tab. 4. Addition of iodine isocyanate to unsaturated fatty compounds.

Nr.	Alkene	Reagent	Product [a]	Yield [%]	Properties	Lit.
1	**2b**	INCO	 **20**	70–75	pale yellow oil	[12]
2	**2b**	1. INCO 2. MeOH	 **20a**	quantitative	viscous oil	[12]
3	**2c**	1. INCO 2. MeOH	 **21a**	77 (crude)	pale yellow oil	[13]

[a] The products were obtained as regioisomeric and racemic mixtures.

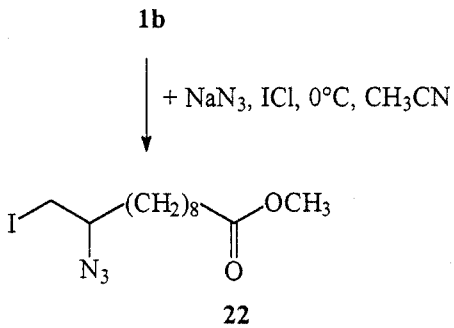
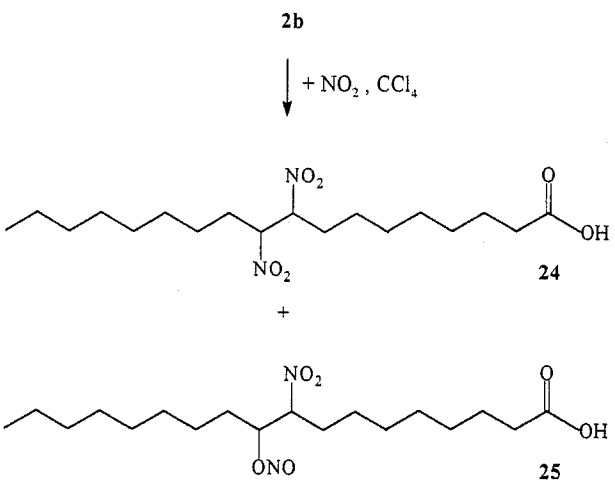


Fig. 5. Addition of iodine azide to methyl 10-undecenoate (**1b**) [16].



+ regioisomer

Fig. 6. Addition of nitrogen dioxide to oleic acid (**2a**) [17].

obtained. NO_2 was reversibly added to the double bond, forming a 2-nitro substituted carbon-centered radical, which gave product **24** by combination with NO_2 and product **25** by combination with the mesomeric nitrito radical. Because of the free rotation possible in this intermediate, the reactions showed no stereospecifity at all. Thus, the products were obtained as a diastereomeric mixture (Tab. 6, Nr. 1). *Vil'yams* and *Vasilev* [18] added NO_2 to petroselinic acid (**3a**) in petroleum ether at 0° C during 9 h and isolated 6,7–dinitrooctadecanoic acid (**26**) and 6(7)-nitrito-7(6)-nitro-octadecanoic acid (**27**). They also investigated the addition of N_2O_3 to petroselinic acid (**3a**) in petroleum ether at 0° C during 8 h and obtained a mixture of 6(7)-nitro-7(6)-nitro-sooctadecanoic acid (**28**) and 6(7)-nitrito-7(6)-nitrosooctadecanoic acid (**29**). Yields and physical data are shown in Tab. 6, entry 2 and 3.

We added NOCl to methyl oleate (**2b**) in dichloromethane in the presence of HCl and obtained the oxime methyl 9(10)-chloro-10(9)-hydroxyiminostearate (**30**) in 84% yield (Fig. 7, Tab. 6, Nr. 4) [19]. The addition of NOCl to oleic acid (**2a**) and methyl ricinoleate (**5b**) has been reported by *Tilden* and *Forster* [20] and *Gupta* et al. [21], respectively.

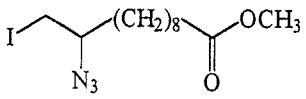
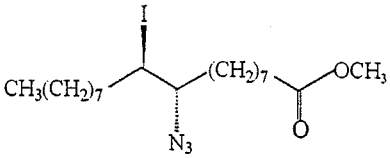
2.4 Addition of N,N-dichlorourethane

The free radical addition of N,N-dichlorourethane to methyl oleate (**2b**) in benzene followed by refluxing in methanol yielded quantitatively the crude methyl 9(10)-(ethylcarbamoyl)-10(9)-chlorooctadecanoate (**31**) as a pale yellow oil (Fig. 8). This reaction was investigated by *Foglia, Maerker,* and *Smith* [15] and shows no stereospecifity because of its free radical character. The resulting β-chloro-carbamates have been used as precursors for the synthesis of methyl 9,10-epiminostearate [15].

2.5 Manganese(III) acetate mediated additions of azide

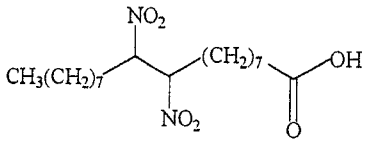
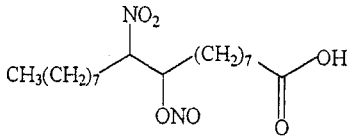
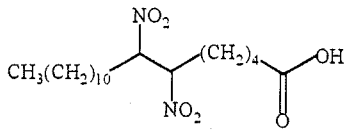
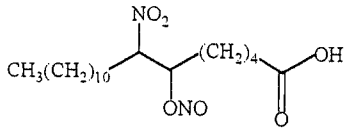
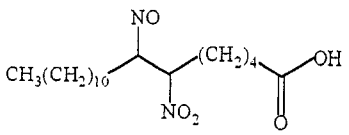
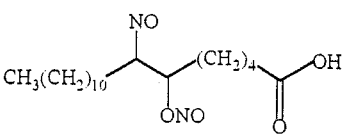
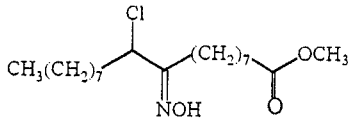
Alkenes can be converted to 1,2-diazides in one step using the manganese(III) acetate mediated addition of azide

Tab. 5. Addition of iodine azide to unsaturated fatty compounds.

Nr.	Alkene	Reagent	Product [a]	Yield [%]	Properties	Lit.
1	**1b**	IN_3	 **22**	quantitative	viscous liquid	[16]
2	**2b**	IN_3	 **23**	quantitative	–	[16]

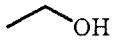
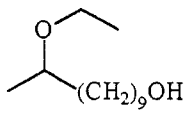
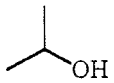
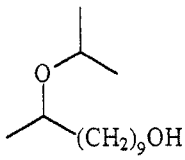
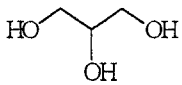
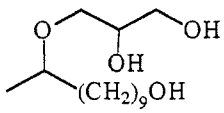
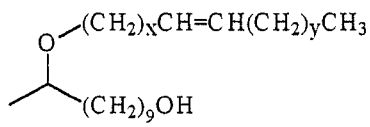
[a] The products were obtained as regioisomeric and racemic mixtures.

Tab. 6. Addition of NO_2, N_2O_3 and NOCl to unsaturated fatty compounds.

Nr.	Alkene	Reagent	Product	Yield [%]	Properties	Lit.
1	**2a**	NO_2	 **24**	24	oil	[17]
			 **25**[a]	43	oil	[17]
2	**3a**	NO_2	 **26**	19	mp. 121–122° C	[18]
			 **27**[a]	64	viscous oil	[18]
3	**3a**	NO_2O_3	 **28**[a]	28	colourless adduct mp. 84–85° C	[18]
			 **29**[a]	68	liquid	[18]
4	**2b**	NOCl	 **30**[a]	84	brown oil	[19]

[a] The products were obtained as regioisomeric mixtures.

Tab. 7. Addition of alcohols **38–41** and **1c** to 10-undecenol (**1c**) in the presence of montmorillonites KSF and K10[a] [35].

Nr.	Alcohol	Product	Yield[d] [%]
1	**38**	**42**[b]	78
2	 **39**	 **43**[b]	61
3	 **40**	 **44**[b]	25
4	 **41**	 **45**[b]	49
5	**1c**	 **46**[b][c]	57

[a] Reaction conditions: Nr. 1–3 were carried out in the presence of KSF, **1c: 38** = 1:4, **1c: 39** and **1c:40** = 1:2, **1c:** KSF = 1:1 (w/w), 90° C, 24 h. Nr. 4 was carried out in the presence of K10, **1c**: **41** = 1:40, **1c**: K 10 = 1:2 (w/w), 90° C, 48 h. Nr. 5 was carried out with **1c**: K 10 = 2:1 (w/w), 90° C, 48 h.

[b] The addition products were obtained as regioisomeric mixtures. Addition occurred with 85–90% at C-10.

[c] x + y = 8.

[d] Products were purified by "Kugelrohr" distillation.

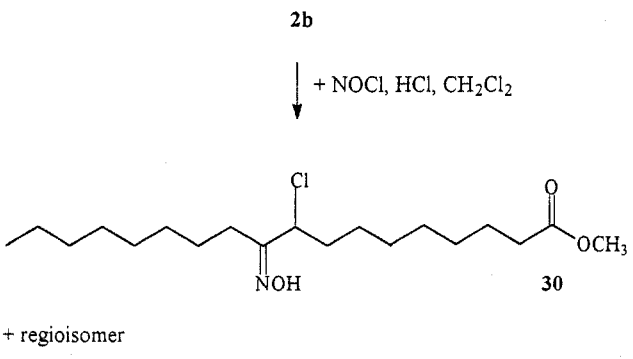


Fig. 7. Addition of nitrosyl chloride to methyl oleate (**2b**) [19].

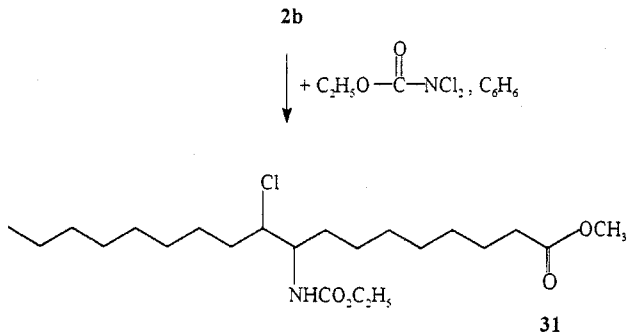


Fig. 8. Addition of N,N-dichlorourethane to methyl oleate **2b** [15].

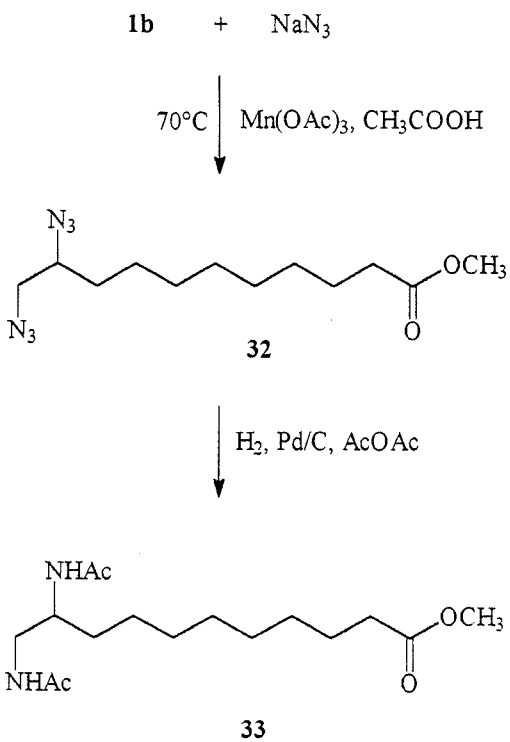


Fig. 9. Manganese(III) acetate mediated addition of azide to methyl 10-undecenoate (**1b**) and catalytic hydrogenation of the addition product **32** in the presence of acetic anhydride.

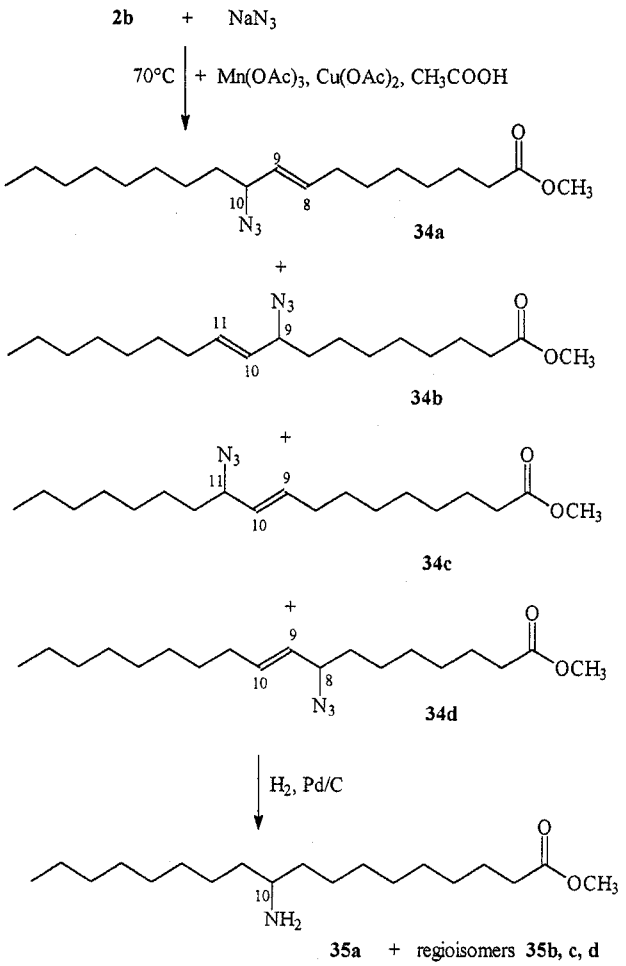


Fig. 10a. Manganese(III) acetate mediated addition of azide to methyl oleate (**2b**) and catalytic hydrogenation of the addition products **34**.

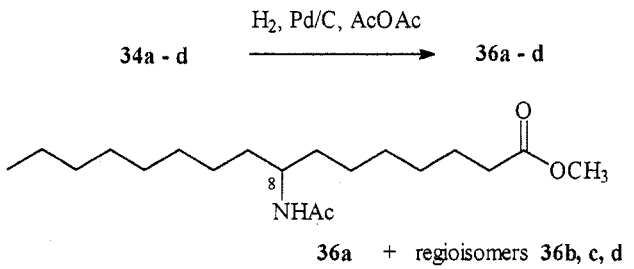


Fig. 10b. Catalytic hydrogenation of addition products **34** in the presence of acetic anhydride.

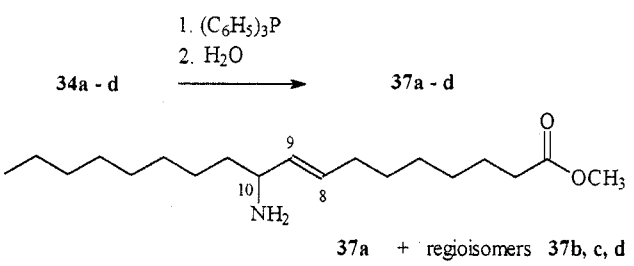


Fig. 10c. Reduction of the addition products **34** using the *Staudinger* reaction.

to the C,C-double bond. The 1,2-diazides were prepared by heating a brown solution of manganese(III) acetate, sodium azide and the alkene in glacial acetic acid until the solution turned colourless, which indicated the reduction of Mn(III) to Mn(II) [22].

This protocol was applied to methyl 10-undecenoate (**1b**) and pure methyl 10,11-diazidoundecanoate (**32**) was obtained after column chromatography in a yield of 27% [23, 24]. The yields can be improved because here an additional product fraction of about 35% was not further purified.

The diazido compound **32** was hydrogenated with Pd/C as catalyst in the presence of acetic anhydride. Methyl 10,11-diacetamidoundecanoate (**33**) was obtained in a yield of 68%. Catalytic hydrogenation of the diazide **32** with Pd/C and without acetic anhydride gave polymeric products (Fig. 9).

Manganese(III) acetate mediated addition of azide to methyl oleate (**2b**) yielded 40% of the unsaturated mono addition product **34** as a mixture of four regioisomers. The yield could be improved to 50% by addition of equimolar amounts of cupric acetate to the reaction mixture [23]. Obviously, the primarily formed addition products **34a,b** are isomerized in a pericyclic rearrangement [25, 26] to give the respective rearranged unsaturated azides. The mixture of regioisomers was catalytically hydrogenated to give a mixture of 8-, 9-, 10- and 11-aminostearates **35** (Fig. 10a). Catalytic hydrogenation in the presence of acetic anhydride yielded the respective isomeric methyl acetamidostearates **36** (Fig. 10b). Alternatively, selective reduction of the azide can also be achieved using the *Staudinger* reaction [27]. Treatment with triphenylphosphine followed by hydrolysis gave the respective methyl aminooctadecenoates **37** (Fig. 10c).

3 Carbon, Oxygen-Bond Forming Additions

3.1 Epoxidation

The epoxidation is one of the most important addition reactions to the double bond of unsaturated fatty compounds. Epoxidations are mostly carried out by reaction with peracids, which are produced *in situ* during epoxidation by interaction of hydrogen peroxide with carboxylic acids or anhydrides or acid chlorides [1, 28]. *Warwel* et al. [29–32] reported chemoenzymatic epoxidations of unsaturated fatty acids and plant oils. In the presence of lipase under treatment with hydrogen peroxide unsaturated fatty acids undergo a two-step chemoenzymatic self-epoxidation and gave the corresponding epoxy fatty acids in yields of 70–90%. Similary, plant oils were epoxidized with yields > 80%.

3.2 Additions of alcohols

Ion-exchanged montmorillonites are known to be effective catalysts for reactions of alkenes with alcohols [33, 34]. Al-exchanged montmorillonite catalyzed reactions of various alkenes with alcohols above and below 100° C have been studied [33]. Montmorillonite clay induced addition reactions of alcohols have been applied to unsaturated fatty compounds [35]. The reaction, e.g. of 10-undecenol (**1c**) and allyl alcohol (**38**), induced by montmorillonite KSF* gave at a reaction temperature of 90° C the ether **42** in an isolated yield of 78% (Fig. 11; Tab. 7, Nr. 1). The corresponding additions of ethanol (**39**) and isopropanol (**40**) afforded the ethers **43** and **44** in yields of 61% and 25%, respectively (Tab. 7, Nr. 2 and 3). The reactions showed a moderate isomerization

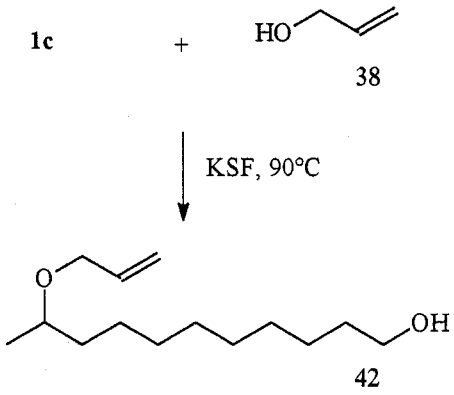


Fig. 11. Addition of allyl alcohol (**38**) to 10-undecenol (**1c**) in the presence of montmorillonite KSF.

and gave the products as regioisomeric mixtures with 85–90% of products resulting from additions to C-10 of the molecule chain. Reactions of alcohols **38–40** with **1c** were also carried out in the presence of montmorillonites K10* and EX 771*. The yields of addition products **42–44** were a little lower than those obtained from the corresponding reactions with KSF. The addition e.g. of allyl alcohol (**38**) gave induced by K10 or EX 771 a 65% (GC) or a 73% (GC) yield of **42**, respectively. In contrast, reaction of **1c** with *tert.* butanol in the presence of K10 yielded 54% of *tert.* butylundecenylether after a reaction time of 4 h. Addition of glycerin **41** to 10-undecenol (**1c**) induced by K10 yielded ether **45** (Nr. 4). Glycerin was used in a 40fold excess.

The unsaturated fatty alcohol **1c** should be able to dimerize via addition of the primary alcohol function to the C,C-double bond. Indeed, at 110° C **1c** gave in the presence of K10 the branched dimeric ether **46** (yield: 57%) with isomerization of the double bond (Tab. 7; Nr. 5). In contrast, at a reaction temperature of 140° C the long chain diundecenylether was obtained (yield: 87%, GC) as a result of the acid catalyzed nucleophilic etherification of the alcohol **1c.**

Additions of alcohols to 1,2-disubstituted alkenes such as oleylalcohol (**2c**) carried out under the same reaction conditions used for **1c** yielded only small amounts of the corresponding addition products. The reaction of **2c** with e.g. alcohol **38** gave 23% (GC) of the respective addition product 9(10)-allyloxyoctadecanol.

Tetrahydrofurans such as **47** (Fig. 12) were obtained from unsaturated fatty compounds e.g. ricinoleic acid (**5a**) by iodoetherification. The cyclization of **5a** was carried out in anhydrous acetonitrile as described by *Bedford* et al. [36] and gave the 3-iodotetrahydrofuran derivative **47** in an isolated yield of 47%. The analogous formation of the 3-bromotetrahydrofuran derivative is described on reaction of ester **5b** with N,N-dibromobenzenesulfonamide [37]. Furthermore, iodoetherifications were applied to homoallylic alcohols obtained by alkylaluminium halide induced ene additions of formaldehyde to unsaturated fatty compounds [38]. The corresponding reaction with the formaldehyde adduct of methyl 10-undecenoate (**1b**) methyl 12-hydroxy-9-dodecenoate gave the respective 2-alkyl-substituted 3-iodotetrahydrofuran derivative in a yield of 50% [39].

* Montmorillonite: KSF is Ca montmorillonite with a low surface area and loaded with sulfuric acid; EX 771 is a porous montmorillonite with a medium surface area and loaded with sulfuric acid and K 10 is a porous clay material with a high surface area, HCl activated and washed acid free.

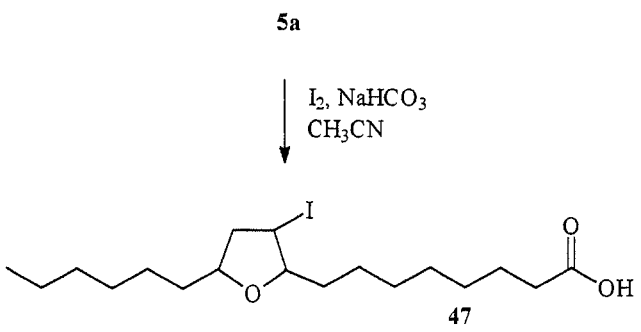


Fig. 12. Iodine-induced cyclization of ricinoleic acid (**5a**).

3.3 Additions of carboxylic acids

Acid catalyzed additions of the carboxyl group of unsaturated fatty acids such as **2a** and **3a** to the double bond of **2a** and **3a**, respectively, afford estolides and/or polyestolides (Fig. 13) [40–43]. Treatment of oleic acid (**2a**) with 1 equiv. of 70% perchloric acid at 50° C yielded after 2 h 76% of polyestolide while the corresponding reaction with concentrated sulfuric acid gave a 65% yield of estolide after 6 h [41]. Recently, the sulfuric acid catalyzed reaction was optimized for minimal acid concentration and lower temperature [42]. The optimal formation of estolide from **2a** was obtained with 5% (v/v) conc. H_2SO_4 at a reaction temperature of 55° C for 24 h under vacuum (yield: 75%). Montmorillonite clay K10 induced condensation of **2a** gave after a reaction time of 118 h at 150° C under nitrogen 32% yield of estolide [41]. The yield could be increased to 41% using an Fe^{3+} cation-exchanged montmorillonite clay. Mainly monoestolide was formed with a small amount of diestolide.

Erhan and *Isbell* [43] also described reactions with montmorillonite clay catalysts, modified to increase their activity for estolide forming reactions from oleic acid (**2a**) and meadowfoam oil fatty acids **7a**. Best yields were obtained with clays activated by Fe^{3+} ions. In a batch reactor, estolide yields increased from 21% with a commercial montmorillonite clay catalyst to 27% with the Fe^{3+} catalyst.

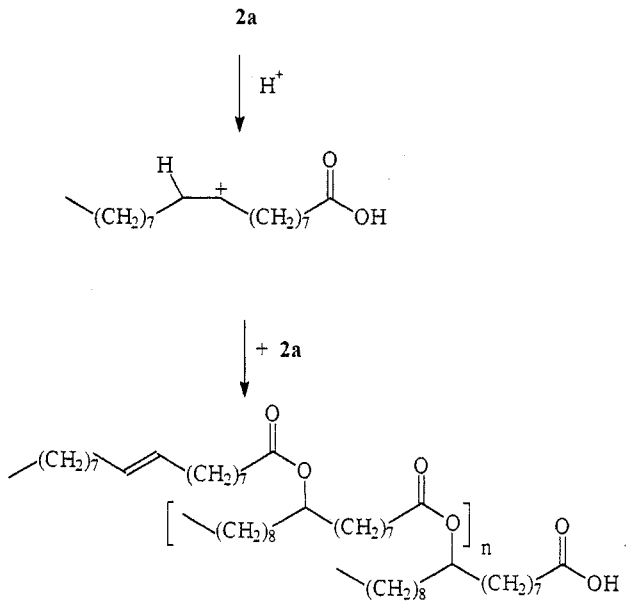


Fig. 13. Acid catalyzed formation of estolides and polyestolides from oleic acid (**2a**) [40].

In contrast, in the presence of mineral acid catalysts such as perchloric and sulfuric acid and polar nonparticipating solvents meadowfoam fatty acids (**7a**) undergo intramolecular cyclizations to give lactones in yields of up to 92% [44]. Acid catalyzed lactonizations especially of short-chain unsaturated acids forming δ- and γ-lactones are reported in literature and summarized by *Isbell* and *Plattner* [44]. γ-Stearolactone was obtained by intramolecular cyclization of oleic acid after isomerization of the double bond induced by 70% perchloric acid [45].

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