

Ane Additions to Unsaturated Fatty Compounds: Thermally Initiated Additions of Alkanes to Methyl 10-Undecenoate *

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Alkanes i.e. cyclohexane, n-heptane and alkylaromatics i.e. toluene could be added to methyl 10-undecenoate to give the respective addition products in a thermally initiated free radical chain reaction (ane-reaction) at supercritical fluid conditions.

The ane reaction is the thermally initiated free radical chain addition of alkanes to the C,C-double bond of alkenes¹. The very first example of the ane reaction was reported in the thirties of this century by *Binapff*². Toluene was added to maleic anhydride to give benzylsuccinic anhydride. The reaction was performed quite easily. A mixture of toluene and maleic anhydride in a ratio of 10:1 was heated in an autoclave for twenty minutes at 300°C to yield 50% of the addition product (Fig. 1). Some comparable examples of the addition of alkylaromatics to maleic anhydride have been reported in literature³.

Almost at the same time the thermal addition of alkanes to ethylene was reported by *Frey* and *Hepp*⁴. The reaction conditions are most remarkable for a carbon-

An-Additionen an ungesättigte Fettstoffe: Thermisch initiierte Additionen von Alkanen an 10-Undecensäuremethylester

Alkane wie Cyclohexan und Heptan und Alkylaromaten wie Toluol wurden unter überkritischen Bedingungen in einer thermisch initiierten Radikalkettenreaktion an 10-Undecensäuremethylester addiert.

carbon bond forming reaction: a temperature of 500°C, a pressure of 500 – 600 bar and a reaction time of 4 minutes.

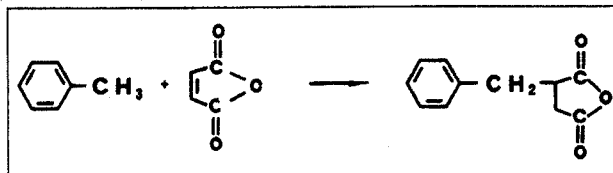


Fig. 1. Addition of toluene to maleic anhydride; reaction conditions: temperature 300°C, reaction time 20 min

We could show that the ane reaction is a very general reaction. Alkanes e.g. cyclohexane could be added in good to moderate yields to electron poor alkenes such as methyl acrylate, acrylonitrile, to styrene and to electron rich alkenes such as 1-octene at temperatures of up to 450°C, a pressure of 200 bar and a reaction time of some minutes. A high excess of the alkane component used as solvent was important. These C,C bond forming reac-

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tions proceed at temperatures of 300°C and up which is the range of thermal cracking of hydrocarbons. Our systematic investigations revealed clearly the reaction mechanism⁵. It is a simple and very effective free radical chain addition reaction (Fig. 2).

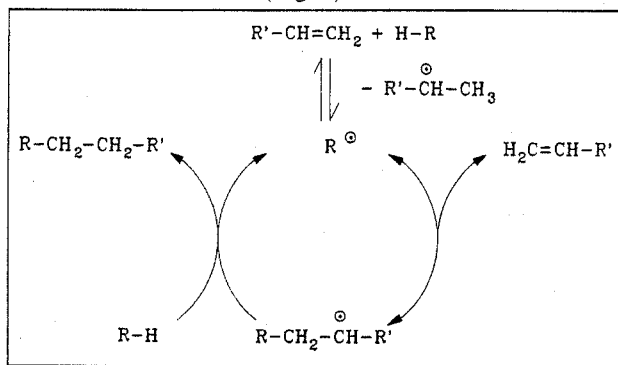


Fig. 2. Mechanism of the ane reaction: free radical chain reaction initiated by comproportionation of alkane and alkene to give two alkyl radicals

The addition of a cyclohexyl radical to the alkene gives the adduct radical, hydrogen transfer from cyclohexane gives the product and cyclohexyl radical to propagate the radical chain. The addition reaction is reversible under the reaction conditions. The radical chain is initiated by a bimolecular reaction of alkane and alkene to give two alkyl radicals; that is the reverse reaction of the well known disproportionation of two alkyl radicals. Addition of a free radical chain initiator is not necessary.

We studied in detail the reaction of cyclohexane and 1-octene to give 1-cyclohexyloctane and – in addition – isomerized octenes⁶. All possible regioisomeric and stereoisomeric octenes were observed.

The isomerization of octene can easily be understood (Fig. 3). In the case of an alkene with allylic C,H bond, radical addition and allylic hydrogen abstraction are competitive reactions. Hydrogen transfer to the adduct radical and to the allylic radical gives the addition product and an isomerized octene, respectively. 1-Octene was reacted almost quantitatively in twenty minutes. The yield of the addition product was about 50 % and 50 % of the 1-octene was isomerized. The ratio of addition and isomerization was approximately 1:1. The ratio of the regioselective addition products 1-cyclohexyloctane and 2-cyclohexyloctane was 96:4.

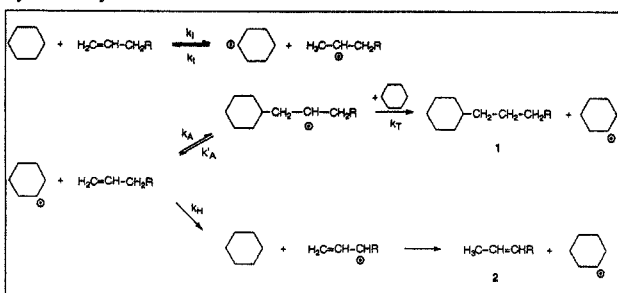


Fig. 3. Mechanism of the addition of cyclohexane to 1-octene: competition of addition and allylic hydrogen abstraction yields addition products as well as isomerization products

Unsaturated fatty compounds are alkenes and should be suitable substrates in the ane reaction. Methyl 10-undecenoate should be comparable to 1-octene as alkene

component in the ane reaction.

A mixture of methyl 10-undecenoate and cyclohexane (weight ratio 1:20) was allowed to react at a temperature of 450°C, and a pressure of 250 bar for two minutes. The conversion of the alkene was approximately 60 % and the yield of the addition product was 50 % based on converted 10-undecenoate. The ratio of the regioisomeric addition products methyl 11-cyclohexylundecanoate and methyl 10-cyclohexylundecanoate was 95:5 and was comparable to the results obtained with 1-octene. Isomerized undecenoates were observed as well. It seems to be remarkable that methyl 11-cyclohexylundecanoate can easily be synthesized by simple addition of cyclohexane to methyl 10-undecenoate (Fig. 4).

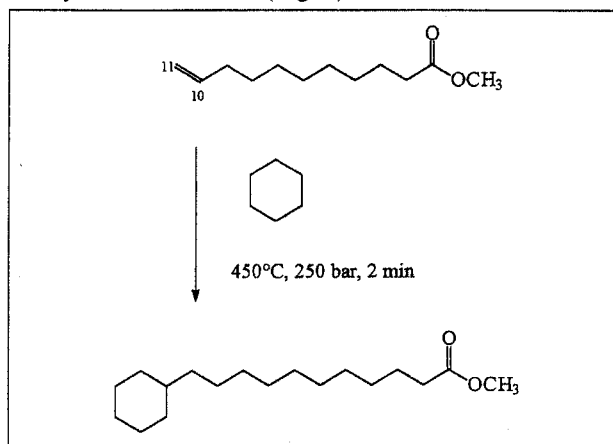


Fig. 4. Addition of cyclohexane to methyl 10-undecenoate to give methyl 11-cyclohexylundecanoate; reaction conditions: temperature 450°C, pressure 200 bar, reaction time 2 min

Addition of n-heptane to methyl 10-undecenoate yielded the expected isomeric stearates. Conversion and yields were comparable to the addition of cyclohexane. All possible regioisomeric addition products were observed and identified unambiguously by GC-MS. The regioselectivity of the addition is remarkable. 50 % of the addition product was formed by addition of C-2 of heptane to the alkene to give methyl 12-methylheptadecanoate (Fig. 5). The regioselectivity of the ane reaction with respect to the alkane has been investigated in detail⁷.

Alkylaromatics such as toluene could be added to methyl 10-undecenoate as well. Methyl 12-phenylundecanoate was synthesized. The conversion of ca. 30 % was lower compared to the addition of alkanes (Fig. 6).

Alkanes and alkylaromatics could be added to oleic acid and erucic acid as well⁷. However, the reaction rate was slower by approximately one order of magnitude compared to 1-alkenes because of the steric effect of the alkyl substituents at the C,C double bond.

The experimental conditions of 450°C, 250 bar and reaction times of 2 min could be realized with a high pressure – high temperature flow apparatus^{5,6,9}. This apparatus is made up of commercially available HPLC-equipment. Operation is extremely simple (Fig. 7). The sample in reservoir 1 is pumped with a high pressure pump 3 into reactor 6 – a stainless steel tube – heated in a GC-furnace. Reaction pressure is maintained with valve 8. Pressure reduction is done in two steps with the valves 8 and 10, which are used also to adjust the flow rate. The product solution is collected in flask 11. The collected solution is distilled.

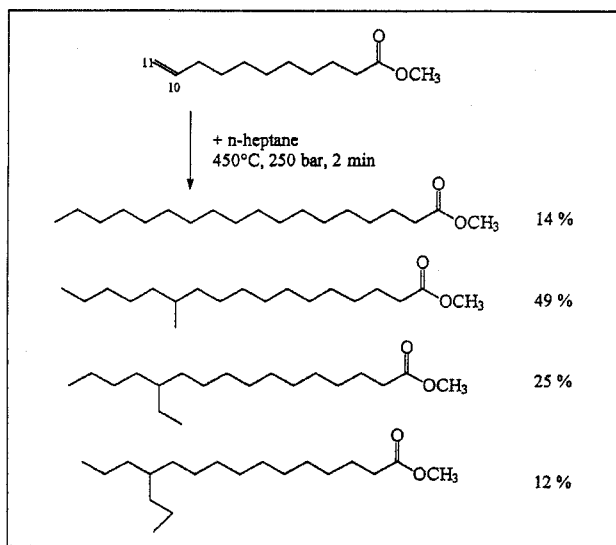


Fig. 5. Addition of n-heptane to methyl 10-undecenoate to give regioisomeric addition products; reaction conditions: temperature 450°C, pressure 250 bar, reaction time 2 min

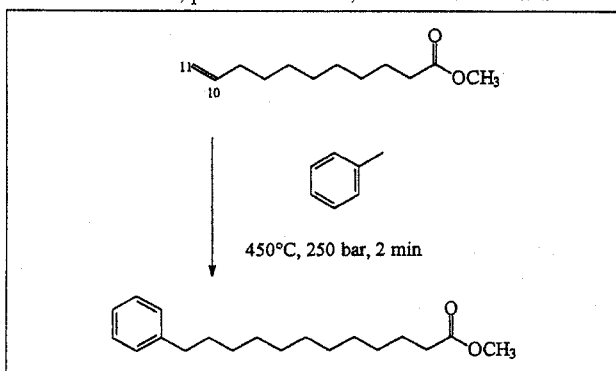


Fig. 6. Addition of toluene to methyl 10-undecenoate to give methyl 12-phenyldodecanoate; reaction conditions as given in Fig. 5

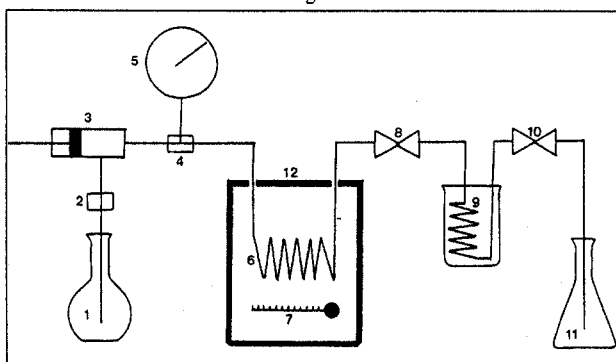


Fig. 7. Schematic diagram of the high pressure - high temperature flow apparatus (HP-HT apparatus); 1) solvent reservoir; 2) filter; 3) high-pressure pump for up to 500 bar; 4) T-piece; 5) manometer for up to 600 bar; 6) reactor; 7) thermometer; 8) heat exchanger (1.6 mm-diameter capillary), 10) valve; 11) collector; 12) furnace

Experimental

Methyl 11-cyclohexylundecanoate

A mixture of 500 ml of cyclohexane and 20 g (0.1 mol) of methyl 10-undecenoate was pumped through the HP-HT apparatus at 450°C and 250 bar with a residence time of 2 min. Cyclohexane was removed. Distillation *in vacuo* through a Vigreux column afforded 12 g of methyl undecenoates (mixture of unreacted methyl 10-undecenoate and isomerized products) and 8.3 g (30%) of colourless methyl cyclohexylundecanoate. Pure methyl 11-cyclohexylundecanoate was obtained by *Spaltrohr* distillation (b.p. 127°C/0.2 torr, n_D^{22} 1.459, m.p. 20.5°C.)

Addition of n-heptane to methyl 10-undecenoate

A mixture of 500 ml of n-heptane and 20 g (0.1 mol) of methyl 10-undecenoate was pumped through the HP-HT apparatus at 450°C and 250 bar with a residence time of ca. 2 min. n-Heptane was removed. Distillation *in vacuo* through a Vigreux column afforded 12.5 g of methyl undecenoates and 7.5 g (25%) of the regioisomeric addition products (b.p. 140–142°C/0.2 torr).

Methyl 12-phenyldodecanoate

A mixture of 500 ml of toluene and 20 g (0.1 mol) of methyl 10-undecenoate was pumped through the HP-HT apparatus at 450°C and 250 bar. Toluene was removed and distillation *in vacuo* afforded 16 g of methyl undecenoates and 2.8 g (10%) of the addition product (b.p. 176°C/0.3 torr, m.p. 19°C, n_D^{22} 1.486).

Literature

- 1 J. O. Metzger, J. Hartmanns and P. Köll, *Tetrahedron Lett.* **22**, 1891 [1981].
- 2 I. G. Farbenindustrie (J. Binapfl), *Deutsches Reichspatent* 607 380 [1935].
- 3 K. Alder and O. Wolff, *Liebigs Ann. Chem.* **576**, 182 [1952].
- 4 F. E. Frey and H. J. Hepp, *Ind. Eng. Chem.* **28**, 1139 [1939].
- 5 J. Hartmanns, K. Klenke and J. O. Metzger, *Chem. Ber.* **119**, 488 [1986].
- 6 J. O. Metzger, *J. Prakt. Chemie* **332**, 767 [1990].
- 7 J. Hartmanns and J. O. Metzger, *Chem. Ber.* **119**, 500 [1986].
- 8 J. O. Metzger and U. Riedner, *Fat Sci. Technol.* **91**, 18 [1989].
- 9 P. Köll and J. O. Metzger, *Angew. Chem.* **90**, 802 [1978]; *Angew. Chem. Int. Ed. Engl.* **17**, 754 [1978].

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