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On the ethenolysis of natural rubber and squalene†‡

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We report here the ethenolysis of squalene and natural rubber utilizing (NHC)(NHC$_{ewg}$)RuCl$_2$(= CRR') and Grubbs–Hoveyda complexes. 0.01 mol% [Ru] per double bond are sufficient for extensive squalene cleavage, resulting in the formation of numerous terminal olefins, which were identified by GC/MS. The depolymerization of natural rubber requires 0.1 mol% [Ru] and leads to the formation of various oligomeric isoprenes, several of which (*n* = 2–6) were isolated and characterized.

The enforced shift from a crude oil-based chemistry to a chemistry relying on renewable resources has initiated vigorous efforts to explore alternatives—primarily plant based substitutes. Consequently, the interest in the conversion of biomass into useful chemicals has grown enormously.[1] Numerous catalytic transformations have been tested on biomass derived saccharides, vegetable oils, animal fats and small terpenes.[2–4] Currently, the most attractive target for olefin metathesis in this context is the conversion of plant oils, primarily methyl oleate,[5,6] utilizing various approaches, such as ethenolysis,[7–12] cross metathesis[13] or enyne metathesis.[14] Polyolefins such as natural rubber, which is isolated from the latex of *Hevea brasiliensis* and various other tropical plants,[15,16] have been neglected—despite the fact that the annual production (2007) of natural rubber amounts to 9.7 × 10^6 t. The crude latex is primarily provided by estates in tropical Asia, with Thailand, Indonesia and Malaysia being the main producers.[17] The high degree of stereoregularity (with respect to double bond geometry and head-to-tail orientation of the repeat units) of natural rubber offers excellent chances for controlled polymer degradation. The cross metathesis reaction[18] of polyolefins with ethene (ethenolysis) depolymerizes macromolecules to smaller isoprene oligomers with terminal double bonds. Due its highly regular stereochemistry, natural rubber should render a small set of terminal olefins (Scheme 3) upon cleavage.

Early pioneering studies by Alimuniar *et al.*[19] and Wagener *et al.*[20] on the ethenolysis of polyisoprenes noted the formation of ill-defined mixtures of partially-depolymerized rubber using tungsten-based olefin metathesis catalysts. The limited success met so far in the ethenolysis of natural rubber is primarily due to the lower reactivity of the trialkylated double bonds. Therefore, the dialkylated double bonds in oleic acid (esters) are much easier targets.[21] We recently developed a series of new (NHC)(NHC$_{ewg}$)RuCl$_2$(CRR′) complexes that are highly active in the formation of sterically-encumbered olefins *via* RCM reactions.[22–25] The key features of such complexes are NHC$_{ewg}$ ligands acting as leaving groups during catalyst initiation.[23] Unlike other NHC ligands, NHC$_{ewg}$ are characterized by electron-withdrawing substituents, which render their electron donation comparable to that of trialkylphosphines.[26,27] The high thermal stability and excellent reactivity of such complexes in olefin metathesis reactions prompted us to test them in the ethenolysis of trisubstituted olefins in squalene and natural rubber.

We first used the linear triterpene squalene ($C_{30}H_{50}$), which is available from olive oil or shark liver,[29] as a model substrate for natural rubber. This is justified as the bond connectivity, double bond substitution and stereochemistry of squalene and natural rubber are very similar. Furthermore, squalene and the partially-cleaved ethenolysis products are well suited for extensive product analysis *via* GC/MS. This facilitates the evaluation of product distribution and enables the optimization of catalysts for later use in natural rubber (NR) and liquid natural rubber (LNR) ethenolysis.

The ethenolysis of squalene dissolved in toluene was initially carried out in the presence of 0.1 mol% of ruthenium complex **1** per double bond. This leads to the full conversion of squalene and the formation of numerous terminal olefins. GC traces of the ethenolysis products of squalene display thirteen major products (Scheme 1).[30] With the aid of GC-MS, all of these

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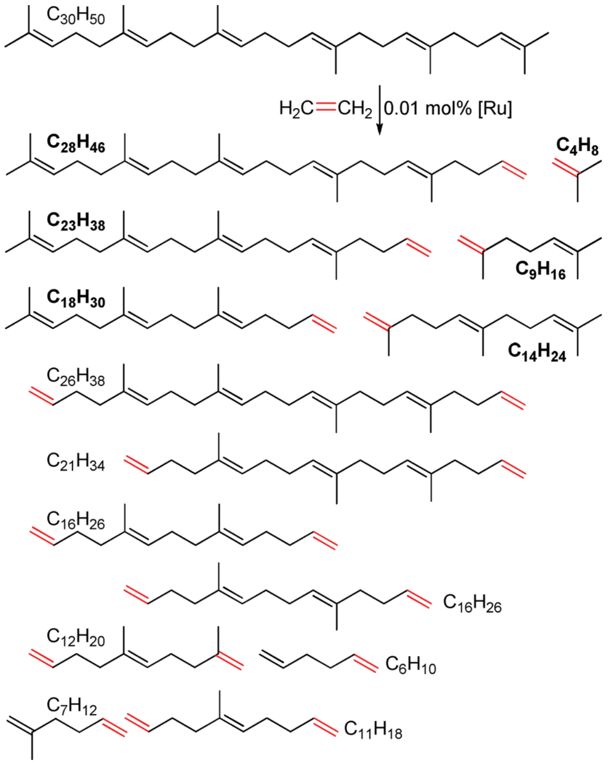
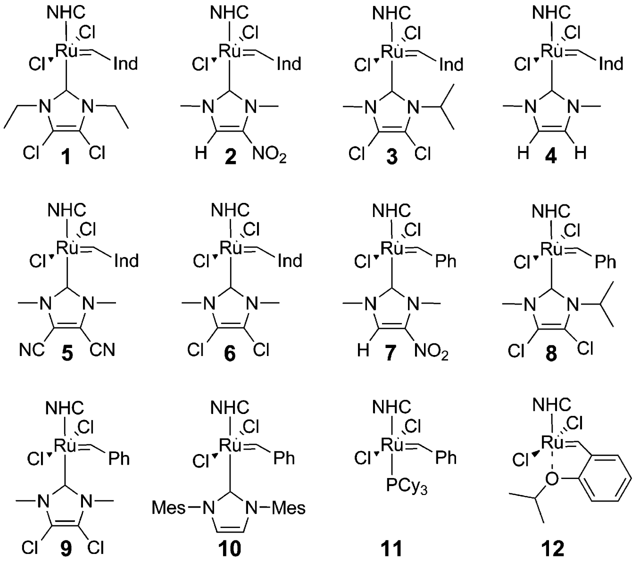
‡ **Ethenolysis of natural rubber or liquid natural rubber:** The rubber (5 g) was placed in a 250 mL Büchi miniclave and toluene (100 mL) added with stirring (dissolving natural rubber requires overnight treatment). Catalyst **1** (63.1 mg, 0.073 mmol, 0.1 mol% per double bond) was added. The reactor was purged with ethene for 5 min, the ethene pressure adjusted to 7 bar and the reactor heated to 120 °C for 3 h. After the reaction, the reactor was allowed to cool to rt and ethyl vinyl ether (0.5 mL) was added for catalyst deactivation. The reaction mixture was transferred to a millipore cell and filtered over a nanofiltration membrane (MWCO 500 Dalton, flow: 1 mL min^{-1}, $\Delta p = 3$ bar) to remove residual polymers. After filtering off *ca.* 80 mL of the solution, toluene (100 mL) was added and a volume of *ca.* 100 mL filtered through the membrane. The toluene was carefully removed from the permeate to obtain *ca.* 3.2 g of residue composed of various oligoisoprenes, which were purified by column chromatography (silica, pentane).



Scheme 1 Ethenolysis of squalene. The bold sum formulas denote the six primary products; eight additional compounds result from ethenolysis of the primary products. All products (except for C_4H_8 and C_6H_{10}) were identified by GC or GC/MS.[28]

were identified (except for the two volatile products: C_4H_8 and C_6H_{10}). As expected for squalene conversions, the primary cleavage products (which require only a single ethenolysis reaction on squalene) are more abundant than the ethenolysis products that result from cleavage of the primary products. The larger amount of $C_{28}H_{46}$ than $C_{23}H_{38}$ indicates that ethenolysis reactions preferably occur in the periphery of squalene and are less likely in the middle of the chain.[31]

In order to optimize squalene ethenolysis, twelve different ruthenium complexes (Scheme 2) were tested in a variety of solvents at different reaction temperatures, squalene concentrations and ethene pressures. Following an extensive optimization (Table 1), a catalyst loading of only 0.01 mol% [Ru] per double bond was found to be sufficient for a 75% conversion of squalene by utilizing catalyst **2** over 3 h at 120 °C, with toluene being the preferred solvent. Notably with catalyst **1**, as little as 0.005 mol% (50 ppm) of [Ru] per double bond enabled 35% squalene conversion (Table 1, entry 11). In contrast to RCM reactions employing (NHC)(NHC$_{ewg}$)RuCl$_2$(CHR) complexes,[23,24] the ideal reaction times for successful ethenolysis reactions were relatively short at elevated temperatures, while longer reaction times led to an increase of secondary products. Obviously, the desired ethenolysis reaction occurs rapidly and other products are not formed in significant amounts (Fig. 1). As noted previously,[7] the effect of ethene pressure is less pronounced, but the reaction slows down at less than 3 bar of ethene and then produces significant amounts of other products.



Scheme 2 Ruthenium complexes tested in squalene ethenolysis (Ind = 3-phenylindenylid-1-ene, NHC = *N*,*N*′-bis(2,4,6-trimethylphenyl)-imdazolinylidene).

In general, the (NHC)(NHC$_{ewg}$)RuCl$_2$(indenylidene) complexes (catalysts **1–6**; Table 1, entries 1 –21) perform better than the related benzylidene complexes (catalysts **7–10**; Table 1, entries 22–27). Grubbs–Hoveyda complex **12** shows an ethenolysis activity comparable to those of complexes **1** and **2**. However, the amount of secondary products formed with **12** is higher than with **1** or **2**.

GC and ^{1}H NMR studies show that the amount of ethenolysis by-products formed with complexes **1** and **2** is small, as long as the reaction solution contains less than 10% weight of squalene. This is in line with the ethenolysis of methyl oleate, but compared to this substrate the cleavage of the squalene double bonds is retarded, while the secondary reaction should occur with equal ease in methyl oleate and squalene ethenolysis. Nonetheless, the concentration of squalene in the reaction solvent appears to be a critical factor. Increasing the amount of squalene to 20% weight in toluene leads to higher conversions, but this also occurs at the cost of significantly enhanced side reactions, such as secondary olefin metathesis and double bond isomerization.[32]

The knowledge obtained in the optimization of squalene ethenolysis was applied to the analogous reactions of natural rubber (SVR 3 L) and liquid natural rubber.[33,34] The major difference between these two materials is that squalene is a small molecule while the latter is a high molecular weight polymeric material. This is also the reason why it is much easier to study and optimize the ethenolysis efficiency of catalysts in squalene reactions. Consequently, the best catalysts for squalene ethenolysis, **1** and **2**, were applied to the ethenolysis of NR and LNR. In order to control the amount of secondary reactions, several such ethenolysis experiments were carried out in C_6D_6 as the reaction solvent. The crude reaction mixture after the ethenolysis reaction was directly probed by ^{1}H NMR spectroscopy. Fortunately, the different types of olefinic protons are easily discerned, based on their chemical shifts. 4.7 ppm ($(–CH_2)(CH_3)C{=}C\underline{H_2}$), 4.90–5.08 ppm ($–CH{=}C\underline{H_2}$), 5.1–5.2 ppm ($CH_2–C\underline{H}{=}C(Me)C$) and 5.75–5.90 ppm ($CH_2{=}C\underline{H}–CH_2$) are the resonances in the olefinic region associated with the regular squalene and natural rubber cleavage products, while resonances

Table 1 Screening results for squalene ethenolysis[a]

			Conditions			
Number	Catalyst	Catalyst (mol%)	Temperature/°C	Time/h	Solvent	Conversion (%)[d]
1	**1**	0.1	100	20	C_6D_6	99
2	**1**	0.1	100	6	C_6D_6	99
3	**1**	0.05	100	6	C_6D_6	82
4	**1**	0.01	100	3	C_6D_6	33
5	**1**	0.01	100	1	C_6D_6	36
6	**1**	0.01	120	3	C_6D_6	65
7	**1**	0.01	120	1	C_6D_6	32
8	**1**	0.01	120	3	Toluene	65
9	**1**	0.005	120	3	Toluene	25
10	**1**	0.005	140	3	Toluene	20
11	**1**	0.005	120	3	Toluene[b]	35
12	**1**	0.005	120	3	Toluene[c]	45
13	**1**	0.005	120	3	CH_2Cl_2	3
14	**1**	0.005	120	3	Pentane	5
15	**1**	0.005	120	3	C_6H_{12}	1
16	**5**	0.005	120	3	Toluene	2
17	**3**	0.005	120	3	Toluene	3
18	**3**	0.01	120	3	Toluene	33
19	**6**	0.005	120	3	Toluene	1
20	**2**	0.01	120	3	Toluene	75
21	**4**	0.01	120	3	Toluene	48
22	**8**	0.01	120	3	Toluene	33
23	**8**	0.005	120	3	Toluene	6
24	**7**	0.005	120	3	Toluene	6
25	**9**	0.01	120	3	Toluene	55
26	**10**	0.005	120	3	Toluene	1
27	**10**	0.005	140	3	Toluene	3
28	**11**	0.01	120	3	Toluene	35
29	**12**	0.005	120	3	Toluene	15
39	**12**	0.01	120	3	Toluene	85[e]

[a] Reaction conditions: Squalene (100 mg) was dissolved in the respective solvent (5 mL), the designated amount of [Ru] was added, the ethene pressure (7 bar) applied and the reaction mixture heated to the designated temperature for the designated time. [b] 8% weight squalene. [c] 20% weight squalene. [d] The conversion was calculated according to conversion = $\text{squalene}_{\text{end}}/\text{squalene}_{\text{start}}$. However, the real TON of the catalyst will be significantly higher, since only ethenolysis reactions on squalene itself are considered, while the ethenolysis of the primary products is not taken into account. [e] Under these reaction conditions, more by-products are formed.

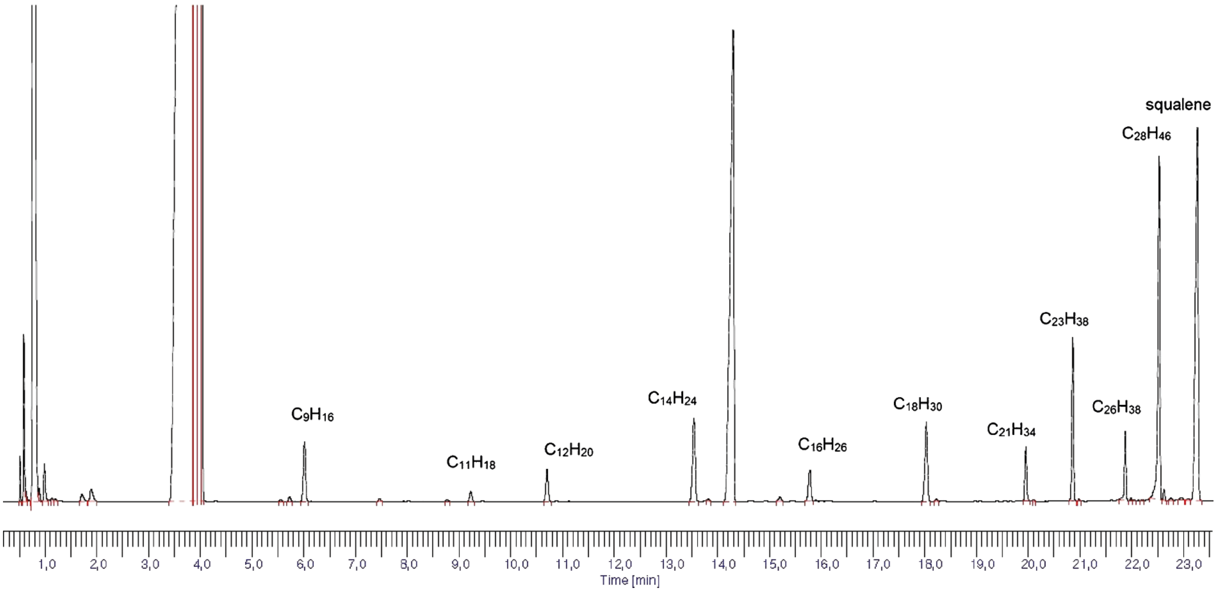


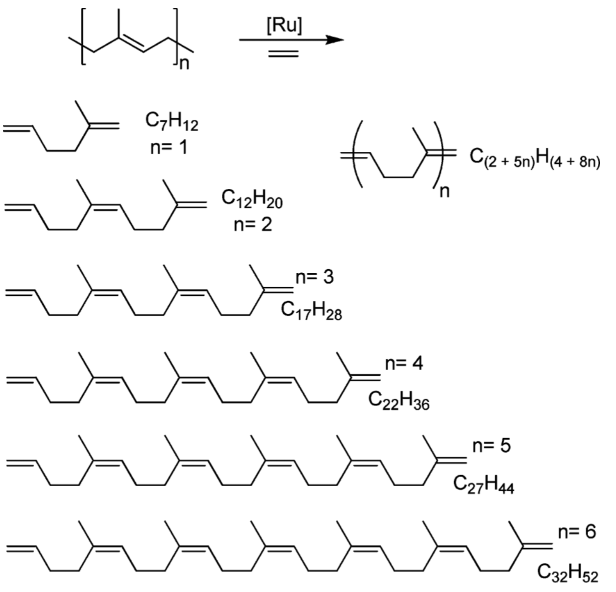
Fig. 1 GC trace of the squalene ethenolysis reaction mixture using complex **1**. The major peaks were assigned with the help of GC/MS (retention time 3.4–4 min: toluene, 14.3 min: tetradecane internal reference).

between 5.3–5.5 ppm represent signals of secondary products with disubstituted double bonds.

An analysis of the ^1H NMR spectra provides clear evidence of the cleavage of NR and LNR. However, the amount of products resulting from secondary reactions, such as double bond isomerization and secondary olefin metathesis,[32] is slightly higher than in the squalene reactions. More importantly, the quantity of catalyst needed for efficient cleavage reactions amounts to *ca.* 0.1 mol% per double bond. This is only partly due to the polymeric nature of the rubber, and it is likely that the need for an increased catalyst loading is related to impurities in NR and LNR.[15–17]

Nonetheless, the relatively high ethenolysis efficiency enables facile multigram depolymerization reactions in toluene using 0.1 mol% of complexes **1** or **2** by applying the conditions reported for squalene.

Following the filtration of the crude reaction mixture over a nanofiltration membrane, a number of ethenolysis products can be separated (Scheme 3) by simple gravity column chromatography. Oligomers ($n = 3$–6) were obtained in >90% purity (HPLC, NMR). The respective products were characterized by ^1H- and ^{13}C-NMR spectroscopy, and high resolution mass spectrometry. Due to the large distance between equivalent groups and the absence of conjugation, the NMR chemical shifts of the various oligomers are fairly similar. An experiment with LNR and NR employing 0.1 mol% of catalyst **1** per double bond provided a *ca.* 65% yield of the short chain oligoisoprenes ($n = 1$ to *ca.* $n = 10$) in the nanofiltration permeate.



Scheme 3 Ethenolysis of natural rubber and the structures of the isolated oligoisoprenes.

Conclusions

We have demonstrated that trisubstituted double bonds in squalene and natural rubber undergo efficient cleavage reactions with ethene catalyzed by 0.1–0.01 mol% $(NHC)(NHC_{ewg})RuCl_2(=CRR')$ complexes per double bond, resulting in the synthesis of several small oligoisoprenes. Future work will be directed towards exploring the up-scaling of the ethenolysis reaction with natural rubber[15] and gutta-percha; tyre rubber especially appears to be an interesting reactant in this respect. Furthermore, the utilization of the oligoisoprenes for the synthesis of flavors, odorants, pheromones and pharmaceutically active compounds will be explored.

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31 This interpretation is based on the (reasonable) assumption of similar GC response factors for these two products.

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