121. Isomerization of Olefins Catalyzed by the Hexaaquaruthenium(2+) Ion

Preliminary Communication

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Isomerization of olefins, in particular the useful transformation of allyl to vinyl ethers is catalyzed by the hexaaquaruthenium(2+) ion, producing the (*E*)-isomers under mild conditions.

Ring-opening metathesis polymerization of strained bicyclic olefins is catalyzed by $[Ru(H_2O)_6]^{2+}$ under mild conditions [1]. Since solvents such as H_2O or EtOH can be used [2] [3], this reaction is attractive with respect to ecological considerations. In analogy to Mo-, W-, or Ti-containing catalysts [4] [5], carbene intermediates have been postulated also for complexes of the iron triad. Experimental evidence for these species has recently been demonstrated for the case of ruthenium phosphines [6]. In the presence of $[Ru(H_2O)_6]^{2+}$, acyclic olefins like allylic ethers and allylic alcohols do not undergo the expected metathesis reaction but show a migration of the C=C bond [3]. In this communication, we report on the range of olefin rearrangements catalyzed by $[Ru(H_2O)_6]^{2+}$ and on the kinetics for specific examples.

Table. *Rearrangement Products*

Substrate[a])	Product[b])	Substrate[a])	Product[b])
Hex-1-ene	(*E*)-Hex-2-ene (87) (*E*)-Hex-3-ene (13)	4-Allyl-1,2-dimethoxybenzene	3,4-Dimethoxy-1-propenylbenzene (> 99)
(*Z*)-Hex-2-ene	(*Z*)-Hex-2-ene (31) (*E*)-Hex-2-ene (31)	4-Allyl-2-methoxyphenole	2-Methoxy-4-propenylphenole (> 99)
	(*E*)-Hex-3-ene (38)	Allyl phenyl ether	Phenyl propenyl ether
(*E*)-Hex-2-ene	(*E*)-Hex-2-ene (59) (*E*)-Hex-3-ene (41)		(> 99)[d])
		Methylidenecyclopentane[c])	Methylidenecyclopentane (60) 1-Methylcyclopentene (40)
(*E*)-Hex-3-ene	(*E*)-Hex-3-ene (90) (*Z*)-Hex-2-ene (10)		
Hex-5-en-1-ol	Hex-5-ene-1-ol (15) Hex-4-ene-1-ol (85)		

[a]) Acyclic olefins which showed no reaction: hex-5-en-2-on, hept-6-enoic acid, 2-methylbut-1-ene, 2-methylbut-2-ene.

[b]) Percentage in brackets; determined by NMR.

[c]) Only successful rearrangement with cyclic olefins. Nonreactive species: methylidenecyclohexane, methylidenecyclobutane, 4-vinylcyclohex-1-ene, vinylcyclohexene.

[d]) Either (*Z*)- or (*E*)-isomer, $^3J_{olefin} = 13$ Hz.

Terminal olefins are converted in high yield into the thermodynamically more stable internal olefins[1]). The process is stereospecific producing the (*E*)-isomer (*Table*), except for (*E*)-hex-3-ene where a small amount of (*Z*)-hex-2-ene is also formed[2]).

We propose the C=C bond migration to proceed *via* formation of an olefin complex of Ru. Facile substitution of one or several H_2O ligands by π-acidic ligands is a well-documented reaction [7] [8]. 4-Allyl-2-methoxyphenole is converted to 2-methoxy-4-propenylphenole by catalytic amounts of $[Ru(H_2O)_6]^{2+}$. The concentration decrease of 4-allyl-2-methoxyphenole with time follows first-order behavior for as long as 5×10^4 s at 31°[3]). This observation is a strong indication that the substitution of one H_2O molecule of $[Ru(H_2O)_6]^{2+}$ by 4-allyl-2-methoxyphenole is the rate-determining step. From the measurement of the temperature dependence of this reaction, the following kinetic parameters are derived: $k^{298} = (3.8 \pm 0.1)\ 10^{-5}\ s^{-1}$, $\Delta H^{\neq} = 44.7 \pm 2\ kJ \cdot mol^{-1}$, and

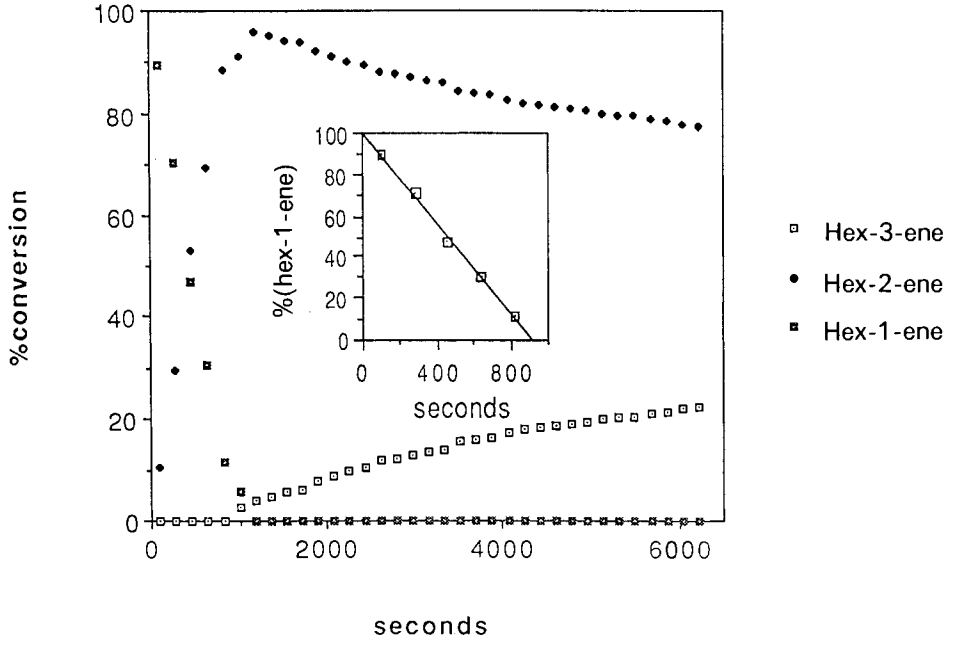

Figure. *Time dependence of the concentration of hex-1-ene, hex-2-ene, and hex-3-ene in the isomerization with* $[Ru(H_2O)_6(tos)_2]$ *as catalyst at 309 K in* $(D_6)EtOH$

[1]) For a typical experiment, 5 mg of $[Ru(H_2O)_6]^{2+}$ was dissolved in 25 µl of D_2O in a NMR tube and diluted with 400 µl of (D_6)EtOH. The olefin (100 µl) was injected, and the NMR tube was kept at 35° for one day. Owing to the facile oxidation of $[Ru(H_2O)_6]^{2+}$, all these operations were carried out under Ar.

[2]) The configuration of the products was determined by observation of ^3J olefinic coupling constants in ^{1}H-NMR ($^3J_Z < 10$, $^3J_E > 13$ Hz) or by comparison with ^{13}C-NMR spectra of the pure substances.

[3]) A typical kinetic run consisted of the following: to 200 µl of a stock solution of 0.0453M $[Ru(H_2O)_6]^{2+}$ in a mixture of (D_6)EtOH/D_2O 15:1 was added 100 µl of olefin. The mixture was then diluted with (D_6)EtOH to a total of 500 µl, and the NMR tube was placed into the thermostated compartment. All solvents were Ar-saturated, and the reactions took place in Ar-filled NMR tubes.

$\Delta S^{\neq} = -180.1 \pm 6.5\ J \cdot K^{-1} \cdot mol^{-1}$. The quite large negative value of $\Delta S^{\neq}$ indicates an associative pathway of the reaction. Further studies will deal with the reaction pathway for this isomerization process and its relation to olefin metathesis.

The same reaction was studied for hex-1-ene. Its concentration decreases linearly with time up to 90% conversion. At this point, the subsequent formation of hex-3-ene begins (*Fig.*). Since hex-2-ene is the only detectable product at the beginning of the reaction, and since its concentration decreases upon formation of hex-3-ene, we conclude that the migration of the C=C bond occurs stepwise, *i.e.* hex-1-ene → hex-2-ene → hex-3-ene.

Rearrangement of allylic ethers and alcohols in aqueous solution [3] with $[Ru(H_2O)_6(tos)_2]$ (tos = *p*-toluenesulfonate) also works in (D_6)EtOH or in THF with $[Ru(H_2O)_6(trif)_2]$ (trif = trifluoromethanesulfonate) [9] as catalysts: our experiments demonstrate that allyl phenyl ether is quantitatively converted to the phenyl vinyl ether at room temperature (12 h) with small amounts of catalyst. This opens applications in organic protecting-group chemistry. The base- and acid-stable allyl derivates of alcohols, acids, or carbonyl compounds can be converted to the corresponding acid-labile vinyl derivates on heating in presence of Pd/C [10] or with tris(triphenylphosphane)rhodium(I) chloride at 60–80° for several hours or leaving the mixture at room temperature for several days [11]. The exceedingly mild reaction conditions with $[Ru(H_2O)_6(trif)_2]$ as well as its solubility in a variety of organic solvents makes it an interesting catalyst for the cleavage of protecting groups *via* isomerization and acid-catalyzed hydrolysis.

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