etry of the molecule (C1–C6: 2.121 Å compared to 2.235 Å in **1**). Apart from that, in the case of **10** one finds an asymmetry in the lengths of the C–C bonds caused by the *peri*-bridge, both in the CH_2 bridge (shortening of C1–C11 to 1.45 Å and lengthening of C6–C11 to 1.51 Å referred to the C1–C11/C6–C11 bond lengths of 1.485 Å in **1**) as well as in the annulene ring; slight deviations from the expected C_s symmetry of the molecule could be due to packing effects (according to studies in collaboration with *J. Lex*). Details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, W-7514 Eggenstein-Leopoldshafen 2 (FRG), on quoting the depository number CSD-55354, the names of the authors, and the journal citation.

[16] Review: F.-G. Klärner, *Top. Stereochem. 15* (1984) 1.

[17] For a detailed discussion of the walk-rearrangement of **9** and **10** see: R. Arnz, *Dissertation*, Universität Köln 1989.

[18] Apart from the mentioned enthalpy effect, the still unknown influence of the *peri*-double bond on the dissociation energy of the C6–C11 bond in **9** has to be taken into account for the difference in reactivity of **9** and **10**. Other than in **9**, the walk-rearrangement initiated by cleavage of the C1–C11 bond also takes place in the case of **10** [$E_A = 43.5 \pm 1.9$ kcal mol^{-1}; $\lg A = 14.4 \pm 0.8$ (gas phase)].

[19] Alternative synthesis of **4**: H. Klenk, W.-D. Stohrer, F. Effenberger, *Chem. Ber. 109* (1976) 777.

Synthesis and Characterization of P-containing ZSM-5 Zeolites

By *Wladimir Reschetilowski,* Brit Meier, Michael Hunger, Baldur Unger,* and *Klaus-Peter Wendlandt*

Zeolites of the Pentasil type can be modified in various ways by incorporation of different elements in the aluminosilicate lattice, both under the conditions of hydrothermal synthesis as well as by post-treatment or impregnation.[1] Often very little is known of the bond order of these elements in the zeolite.

The aim of the present study was to prepare a series of P-containing zeolites with ZSM-5 structure (P-ZSM-5) by direct synthesis and to characterize them NMR spectroscopically as well as by adsorptive and catalytic measurements.

Silicon-rich P-ZSM-5 zeolites with variable P content were synthesized in laboratory autoclaves under the conditions used for the synthesis of ZSM-5[2] by hydrothermal crystallization of a reaction mixture of water glass, aluminum sulfate and phosphoric acid with the addition of *n*-propylamine. The reaction temperature was 170 °C and the duration of crystallization 55 h. The product was thoroughly washed with distilled water, dried, and tempered at 500 °C over the course of 6 h. The freshly calcined product was converted into the H-form by ion-exchange with a 0.5 N NH_4NO_3 solution at 80 °C for 3 h. The ion-exchange was followed by thermal deammonization at 500 °C over the course of 4 h.

The composition of the modified P-ZSM-5 zeolite was determined by electron probe microanalysis and with the help of ^{27}Al-MAS-NMR spectroscopy (MAS = magic angle spinning). The measurement of the isopiestic H_2O adsorption capacity of the sample tempered at 500 °C was performed at 20 °C. The catalytic properties of the P-ZSM-5 zeolites in the H-form were investigated in the acid-catalyzed cracking reaction of *n*-hexane in an integral flow reactor at normal pressure and at a reaction temperature of 300 °C. Taking a first-order rate law as basis, reaction rate constants could be determined which were used to establish the catalytic activity and the tendency of zeolite samples employed to deactivate according to the equation $1/k = 1/k_0 + B\tau$[3] (k and k_0 = reaction rate constants at time τ and $\tau = 0$; τ = time on stream; B = deactivation parameter).

The P contents, Si/Al ratios, results of adsorption and ^{1}H-MAS-NMR investigations and the catalytic measurements are summarized in Table 1.

Table 1. P-ZSM-5 zeolites investigated in the H-form and results of the adsorption, ^{1}H-MAS-NMR and catalytic measurements.

Sample No.	P per unit cell	Si/Al	A_{H_2O} [cm^{3}g^{-1}]	SiOH/POH [10^{19}g^{-1}]	Si–OH–Al [10^{19}g^{-1}]	k_0[a]	B[b]
1	0	15	0.19	10	50	1.71	0.005
2	0.14	30	0.18	8.5	38	0.51	0.032
3	0.4	31	0.16	11	41	0.36	0.043
4	0.5	30	0.16	13	37	0.28	0.089
5	0.8	30	0.14	10	38	0.12	0.355

[a] k_0 = rate constant at time $\tau = 0$ in mol MPa^{-1}g^{-1}h^{-1}. [b] B = deactivation factor in MPa g mol^{-1}.

The ^{31}P-MAS-NMR signal of the P-ZSM-5 samples synthesized is shifted to lower range compared to the ^{31}P-NMR signal of H_3PO_4 and lies at $\delta = -2.5$. Together with the significantly reduced H_2O adsorption capacity in the samples with the highest P content this can be regarded as a further indication that the phosphate groups in the synthesized products are linked to the aluminosilicate framework preferentially in the form of dihydrogen phosphate groups. Hence, the geminal P–OH groups protruding into the channeling of the framework fill a part of the pore volume which would otherwise be available for an unhindered H_2O adsorption.

^{1}H-MAS-NMR measurements show that the phosphorus-free reference sample (Sample 1) contains bridging OH groups ($\delta = 4.2 \pm 0.1$) in a concentration of 50×10^{19} g^{-1} (Table 1). The concentration of the SiOH/POH groups ($\delta = 2.0 \pm 0.2$), whose differentiation is not possible, is 10×10^{19} g^{-1} and hardly changes on transition to P-containing ZSM-5 zeolites (Samples 2 to 5); the concentration of bridging OH groups clearly increases thereby to 40×10^{19} g^{-1} independently of the P content.

It seems plausible that the bridging OH groups determine the catalytic activity in proton-catalyzed reactions since the reference sample, which has the largest concentration of Si–OH–Al groups, shows the highest catalytic activity in the cracking of *n*-hexane (Table 1). It seems surprising at first sight that the P-ZSM-5 samples exhibit differing catalytic activity despite the almost equal concentration of acidic OH groups: an increase in the P content in P-ZSM-5 zeolites with unchanged Si/Al ratio in the zeolite framework leads to a reduction of the catalytic activity and a poorer activity-time behavior. Apparently the acid-strength distribution of the acidic OH groups is shifted more and more in favor of weakly acidic Brønsted acid centers with increasing P content, and results in a reduced catalytic activity. This explanation is consistent with the observation of *Lercher* et al.[4] that the concentration of strongly acidic Brønsted acid centers decreases and that of the weakly acidic centers increases when the number of the dihydrogen phosphate groups in the zeo-

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lite surface is increased. This then also explains the increased tendency to deactivation observed on the P-ZSM-5 zeolite samples investigated. Both a rapid "fatiguing" of the catalytically active centers as a result of coking as well as blocking of the pores following deposition of coke can be regarded as the cause of the rapid deactivation at high P contents in the zeolite.

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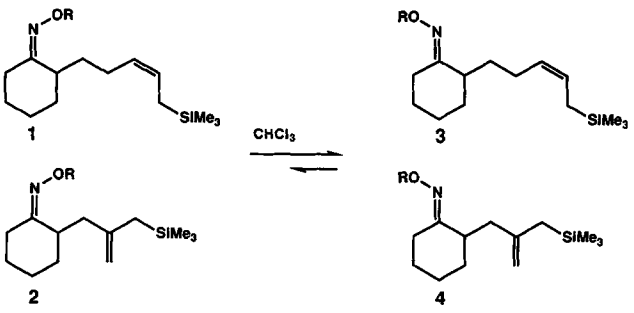
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H_2O, 7732-18-5; water glass, 1344-09-8; aluminum sulfate, 10043-01-3; phosphoric acid, 7664-38-2; *n*-propylamine, 107-10-8; *n*-hexane, 110-54-3.

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Synthesis of Heterocycles by Tandem Reactions: Beckmann Rearrangements/Allylsilane Cyclizations**

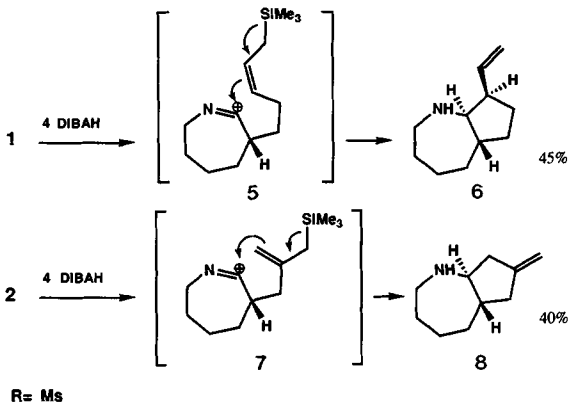
By *Dieter Schinzer** and *Yunxin Bo*

Diastereoselective cyclization reactions leading to five- to eight-membered rings by intramolecular Sakurai reactions have proven to be a very useful preparative strategy.[1] Herein, we now describe for the first time the use of this method for the synthesis of heterocycles by tandem reactions of functionalized oximes. The starting compounds necessary for this purpose, such as **1** and **2** (R = H), are readily accessible by alkylation of simple oximes.[2] By stirring in chloroform (acid actalysis) they can also be converted into the (*E*)-configurated isomers **3** and **4**, respectively ((*Z*) : (*E*) ratio ca. 2.5 : 1). Reaction with mesyl chloride affords the corresponding methanesulfonates **1**–**4** (R = Ms).



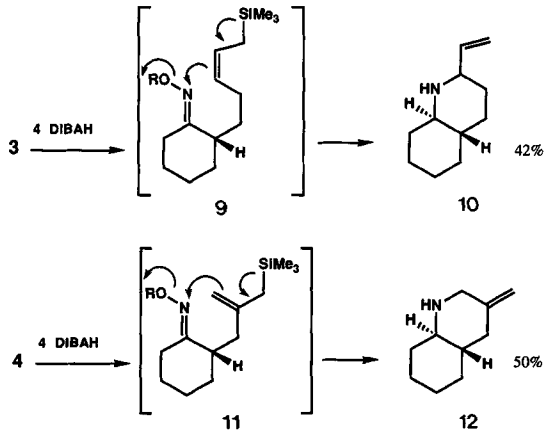
When the compounds **1** and **2** (R = Ms) are allowed to react with four equivalents of DIBAH[3] (diisobutylaluminum hydride) in methylene chloride at low temperature (−78 °C to 0 °C), the heterocycles **6** and **8**, derivatives of azepane, are obtained in a tandem reaction.

In this reaction sequence DIBAH apparently reacts initially as a mild Lewis acid and induces a stereoselective Beckmann rearrangement[4] to give the ring-expanded intermediates **5** and **7**, which are trapped in situ and regioselectively by the electron-rich allylsilane. In the last reaction step the imines are reduced stereoselectively to the secondary amines **6** and **8**, respectively. We are thus in a position to prepare precursors for the syntheses of azepine alkaloid systems stereoselectively in a one-pot reaction.[5]



The analogous reaction of the (*E*)-configurated oximes **3** and **4** leads, when R = Ms, to their decomposition; in contrast, with R = H we surprisingly isolated **10** and **12**, heterocycles of the perhydroquinoline type, and not the expected 1,3-annelated products. Apparently the allylsilane-cyclization is now more rapid than the Beckmann rearrangement—in contrast to **1** and **2**, where, for steric and stereoelectronic reasons, a Beckmann rearrangement takes place first—so that the oxime nitrogen atom is now incorporated directly into the ring being formed. This is to our knowledge the first case in which an allylsilane reacts with a positively charged nitrogen atom.

Here too, a polarization of the NO bond by DIBAH most likely takes place first. In the cyclization step the Beckmann rearrangement cannot compete with the allylsilane cyclization; it is therefore suppressed and the cyclization to the six-membered ring ensues via the intermediates **9** and **11**. Subsequently, these are reduced in situ to give the heterocycles **10** and **12**, respectively.[5–7]



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