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[10] **7a**: ^{1}H NMR (270 MHz, $CDCl_3$): δ = 8.68 (d, 1H, *J* = 8.9 Hz, Ph), 7.94 (d, 1H, *J* = 8.9 Hz, Ph), 7.80–7.67 (m, 3H, Ph), 7.61–7.52 (m, 3H, Ph), 7.39 (ddd, 1H, *J* = 6.9, 6.9, 1.3 Hz, Ph), 7.17 (d, 1H, *J* = 8.9 Hz, Ph), 6.14 (d, 1H, *J* = 2.0 Hz, C12-H), 5.74–5.62 (m, 1H, C11-H), 5.53, (br. d, 1H, *J* = 5.0 Hz, C5-H), 5.39 (ddd, 1H, *J* = 16.8, 1.3, 1.3 Hz, vinyl), 5.18 (ddd, 1H, *J* = 9.9, 1.3, 1.3 Hz, vinyl), 4.52 (d, 1H, *J* = 3.6 Hz, C10-H), 4.07 (br. d, 1H, *J* = 5.3, 5.0 Hz, C4-H), 3.00 (d, 1H, *J* = 18.1 Hz, C8-H), 2.73 (dd, 1H, *J* = 18.1, 1.0 Hz, C8-H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ = 169.7, 167.3, 164.5, 137.5, 134.1, 132.1, 131.7, 131.6, 131.1, 130.8, 129.4, 129.1, 129.06, 129.0, 128.6, 127.9, 125.1, 123.9, 119.8, 119.2, 104.1, 100.2, 98.6, 94.6, 86.8, 86.3, 83.8, 83.4, 69.5, 45.9, 27.7; IR ($CHCl_3$): $\tilde{\nu}$ = 3414, 2924, 2210, 1722, 1640, 1463, 1283, 1240, 1138, 947, 831 cm^{-1}; FAB-MS: *m/z*: 563 [M^+ − H].

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[12] **7b**: ^{1}H NMR (270 MHz, $CDCl_3$): δ = 8.01 (br. d, 1H, *J* = 8.9 Hz, Ph), 7.89 (d, 1H, *J* = 2.3 Hz, Ph), 7.81–7.77 (m, 1H, Ph), 7.67–7.64 (m, 1H, Ph), 7.56 (ddd, 1H, *J* = 7.6, 7.6, 1.7 Hz, Ph), 7.51 (ddd, 1H, *J* = 7.6, 7.6, 1.7 Hz, Ph), 7.00 (d, 1H, *J* = 8.9 Hz, Ph), 6.86 (br. d, 1H, *J* = 2.3 Hz, Ph), 6.08 (d, 1H, *J* = 2.3 Hz, C12-H), 5.68 (dd, 1H, *J* = 3.6, 2.3 Hz, C11-H), 5.67 (ddd, 1H, *J* = 16.8, 9.9, 5.9 Hz, vinyl), 5.53 (br. d, 1H, *J* = 5.3 Hz, C5-H), 5.39 (br. d, 1H, *J* = 16.8 Hz, vinyl), 5.18 (br. d, 1H, *J* = 9.9 Hz, vinyl), 4.52 (d, 1H, *J* = 3.6 Hz, C10-H), 4.40 (br. dd, 1H, *J* = 5.9, 5.3 Hz, C4-H), 3.84 (s, 1H, OMe), 2.98 (br. d, 1H, *J* = 17.8 Hz, C8-H), 2.72 (dd, 1H, *J* = 17.8, 1.3 Hz, C8-H), 2.56 (s, 1H, Me); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ = 172.1, 169.2, 167.2, 164.0, 159.5, 136.9, 134.6, 134.0, 133.0, 132.2, 131.8, 131.2, 130.6, 130.1, 129.4, 129.2, 127.9, 123.1, 119.8, 116.6, 115.8, 104.3, 103.8, 100.4, 94.8, 87.1, 86.0, 83.7, 83.6, 83.3, 69.5, 55.2, 46.1, 27.4, 20.0; IR ($CDCl_3$): $\tilde{\nu}$ = 3410, 2924, 1724, 1634, 1614, 1464, 1412 ,1376, 1283, 1174, 1150, 1119, 991, 955 cm^{-1}; FAB-MS: *m/z*: 607 [M^+ − H], 631 [M^+ + Na].

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Synthesis and Catalytic Activity of Dendritic Diphosphane Metal Complexes

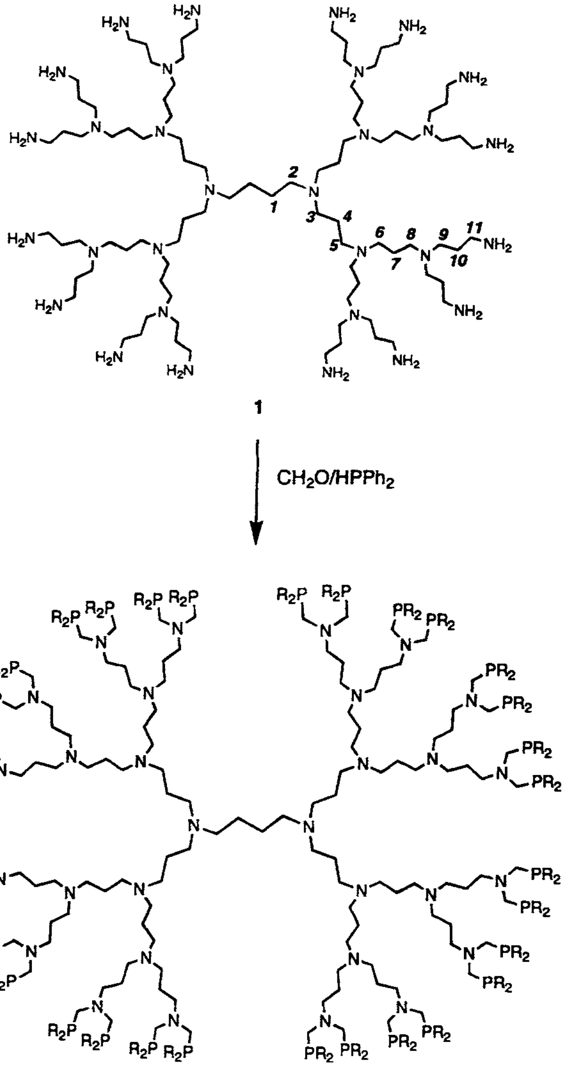
Manfred T. Reetz,* Gunther Lohmer, and
Renate Schwickardi

Dedicated to Professor Dieter Seebach
on the occasion of his 60th birthday

The synthesis of dendrimers with defined inner and outer structural elements provides access to macromolecular materials having special properties and functions[1] that are, in principle, also useful for applications in catalysis. Although a number of metal-containing dendrimers have been described,[1, 2] they were rarely prepared for use as catalysts.[3–5] As recently delineated by van Koten et al., such catalysts can be considered to be at the interface between homogeneous and heterogeneous catalysis.[3] In the most favorable case they combine the advantages of both classes of catalysts, namely, the existence of a specific number of structurally defined, catalytically active metal centers as in traditional homogeneous catalysis as well as the possibility of simple separation and reuse of the catalyst as in heterogeneous catalysis. However, recycling has not yet been achieved for any dendritic metal catalyst.

We now report on 1) a simple synthesis of dendritic diphosphanes, 2) the preparation of the corresponding metal and bimetal complexes, 3) their application in catalysis, and 4) modes of recycling the dendritic metal catalysts.

The starting point of our synthesis is the DAB-based (DAB = 1,4-diaminobutane) polyamino dendrimer DAB-dendr-$(NH_2)_{16}$ (**1**), which can be prepared according to the method of Vögtle et al.,[6] and which is now commercially available.[7] Double phosphinomethylation of each of the 16 primary amino endgroups, a reliable reaction type in simple cases,[8] was effected in essentially quantitative yield upon use of Ph_2PCH_2OH prepared in situ from CH_2O and $HPPh_2$. The reaction affords the dendrimer DAB-dendr-$[N(CH_2PPh_2)_2]_{16}$[9] (**2**), which has a molecular weight[10] of 8029; it was characterized by elemental



2 (R = C_6H_5)

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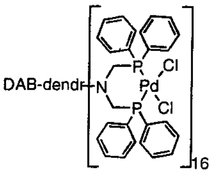
analysis as well as IR and NMR spectroscopy. For example, during the course of the reaction the NH bands in the IR spectrum disappeared completely. The ^{13}C NMR spectra of **1** and **2** are also instructive (Figure 1). In particular, the signals at $\delta = +30.6$ and $+40.3$, corresponding to the C10 and C11 atoms of **1**, are no longer visible in the spectrum of the phosphinomethylated compound **2**, which is a clear indication of a quantitative reaction mode. The completeness of the double phosphinomethylation is also evident by inspection of the ^{31}P NMR spectrum of **2**. It shows a sharp signal at $\delta = -28.0$ and resembles the spectrum of the parent compound $n\text{-}C_3H_7\text{-}N(CH_2PPh_2)_2$ ($\delta = -27.8$).

Figure 1. Portions of the ^{13}C NMR spectra of **1** (top) and of **2** (bottom).

The dendrimer **2** with 16 bidentate ligands on the outer surface provides the possibility of specific complexation with a variety of transition metals, and loading can be complete or partial. In an initial series of experiments complete metal loading forming the metal-containing dendrimers **3**–**6** was readily accomplished under standard reactions with $[PdCl_2(PhCN)_2]$, $[Pd(CH_3)_2(tmeda)]$, $[Ir(cod)_2BF_4]$ and $[Rh(cod)_2BF_4]$. For the purpose of characterization, correct elemental analyses and particularly NMR spectroscopy were useful, especially as NMR data of the corresponding metal complexes of the parent compound $n\text{-}C_3H_7N(CH_2PPh_2)_2$ were available for comparison: the ^{31}P NMR data of the model compounds and of the dendrimers do not differ significantly ($\delta = +8.3$ for **3** and $+8.5$ for $[n\text{-}C_3H_7\text{-}N(CH_2PPh_2)_2PdCl_2]$; $+3.3$ for **4** and $+3.9$ for $[n\text{-}C_3H_7\text{-}N(CH_2PPh_2)_2Pd(CH_3)_2]$; $+7.6$ (d, $J_{P,Rh} = 141$ Hz) for **6** and $+7.8$ (d, $J_{P,Rh} = 141$ Hz) for $[n\text{-}C_3H_7N(CH_2PPh_2)_2\text{-}Rh(cod)BF_4]$).



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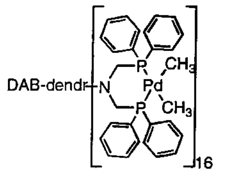

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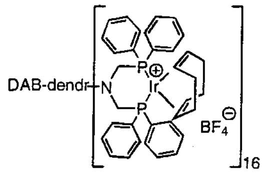

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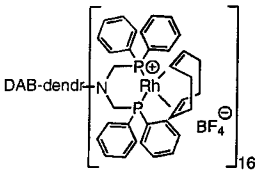

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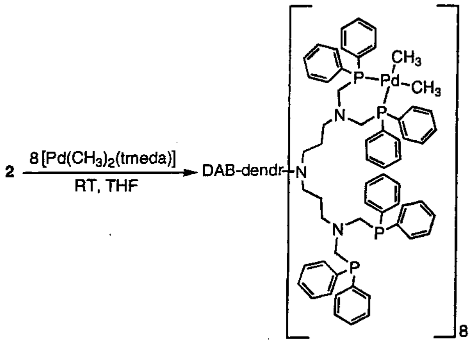
To prepare bimetallic complexes, dendrimer **2** was first loaded with $[Pd(CH_3)_2(tmeda)]$ to 50%. Due to the statistical distribution of the metal, the formation of a single defined product **7** is unlikely. The ^{31}P NMR spectrum of the crude product shows two sharp signals at $\delta = -27.8$ and $+3.5$ for the metal-free and the metal-containing ligands, respectively. Upon reacting the material with $[Ni(CH_3)_2(tmeda)]$, bimetallic dendrimers **8** were obtained. The ^{31}P NMR spectrum reveals two signals at $\delta = +3.5$ and $+18.5$.



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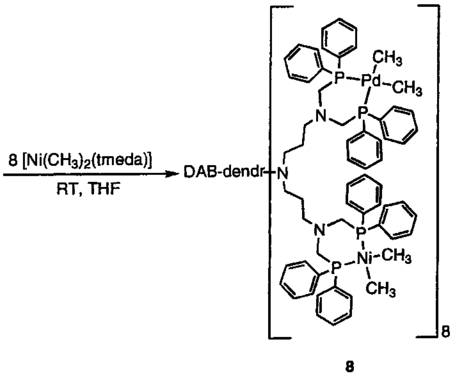

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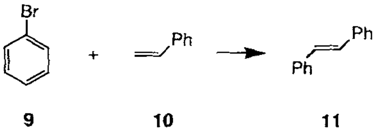
Initial experiments to test the metal-containing dendrimers in catalysis were successful, for example, in the Heck reaction[11] of bromobenzene **9** and styrene **10** with formation of stilbene **11**.

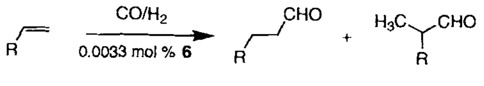


9 **10** **11**

Reactants **9** and **10** were dissolved in dimethylformamide (DMF) and heated for 3 h at 130 °C in the presence of sodium acetate as base and complex **4** (0.125 mol% corresponding to 2 mol% "Pd-monomer") as catalyst. The insoluble inorganic components were filtered from the reaction mixture, and the clear solution was diluted with diethyl ether. Addition of this relatively unpolar solvent caused essentially complete precipitation (>98%) of a Pd-containing dendrimer, the precise structure of which has not been determined.[12] The analysis of the reaction mixture by gas chromatography showed the presence of **11** (89%) and 1,1-diphenylethylene (11%) at a conversion of 85–90%. The isolated Pd-containing dendrimer was used in the same reaction once more and displayed comparable catalytic activity (91% **11** and 9% 1,1-diphenylethylene, conversion 77%). The catalytic activity of the precatalyst **7** having 50% Pd-loading was similar.

In the few previously known cases of catalysis with dendritic metal complexes, catalytic activity was shown to be slightly or significantly lower than that of the corresponding monomeric parent compounds.[3, 4] In contrast, we observed in our system a significantly higher activity (typically, turnover numbers (TON) of 50 for **4** versus 16 for the parent compound $[RN(CH_2PPh_2)_2Pd(CH_3)_2]$, R = n-C_3H_7 or C_6H_5). This is attributable to the higher thermal stability of the dendritic complexes. Thus, in the case of **4** and **7** practically no undesired formation of elemental Pd was observed. In contrast, the Pd complexes of the parent compounds undergo partial decomposition with formation of Pd precipitates.

Finally, in preliminary experiments the hydroformylation[13] of 1-octene **12** was tested. Use of 0.0033 mol% (0.052 mol% "Pd-monomer") of the Rh-containing dendrimer **6** and a small excess (5%) of the free ligand **2** gave a smooth reaction with quantitative formation of the aldehydes **13** and **14** in a ratio of 60:40 (turnover frequency (TOF) = 360 h^{-1}). These data are similar to the values obtained upon using the parent compounds $[PhN(CH_2PPh_2)_2Rh(cod)BF_4]$ or $[n\text{-}C_3H_7N(CH_2PPh_2)_2\text{-}Rh(cod)BF_4]$ (TOF = 240 h^{-1}; *n*/*iso* = 62:38 and TOF = 185 h^{-1}; *n*/*iso* = 61:39, respectively).[14] Although an efficient method for recycling the very small amounts of the dendritic catalyst still needs to be developed, several options are evident. The use of membrane reactors[15] is a perspective that is also of interest for the other metal-containing dendritic catalysts described herein.



14 R = C_6H_{13} **15** **16**

The strategy that we have developed for the synthesis of dendritic diphosphanes opens a general way to prepare transition-metal-containing dendrimers for use in catalysis. Thus, dendrimer **1** was treated analogously with $CH_2O/HP(cyclo\text{-}C_6H_{11})_2$ or $CH_2O/HP(C_2H_5)_2$ to provide the corresponding dendrimers with 16 outer cyclohexyl- or ethyl-substituted diphosphane units. The corresponding $[Pd(CH_3)_2]$ and $[Rh(cod)BF_4]$ complexes were also prepared analogously and are currently the subject of further investigations, as are diphosphane-metal complexes of the commercially available polyamino-dendrimer DAB-dendr-$(NH_2)_{64}$[7] having 64 outer amino groups.

Experimental Section

Synthesis of dendrimer **2**: Under an inert atmosphere the mixture of paraformaldehyde (0.213 g, 7.09 mmol) and diphenylphosphane (1.35 mL, 7.76 mmol) in methanol (5 mL) was heated at 65–70 °C for 10 min. The reaction mixture was cooled to room temperature and treated with a solution of **1** (0.336 g, 0.20 mmol; 3.19 mmol with respect to the amino endgroups) in methanol (3 mL). After 0.5 h stirring at room temperature, toluene (15 mL) was added, and the clear yellow solution heated at 65 °C for 0.5 h. To ensure complete reaction, the mixture was stirred for an additional 12 h at room temperature. The volume of the reaction mixture was concentrated under reduced pressure to about 3 mL, and methanol (10 mL) was added. The product precipitated in the form of a glassy colorless solid, which was dried under high vacuum for 10 h at 60–65 °C. Yield: 1.53 g (>96%). IR (KBr): $\tilde{\nu}$[cm^{-1}] = 3068 (phenyl), 3050 (phenyl), 2941 (NCH_2), 2793 (NCH_2), 1484 (phenyl), 1479 (phenyl), 1432 (phenyl), 739 (phenyl), 693 (phenyl). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.45 (m, 60 H, $NCH_2CH_2CH_2N$, $NCH_2CH_2CH_2CH_2N$), 2.18 (m, 52 H, $CH_2NCH_2CH_2$), 2.34 (m, 32 H, $NCH_2CH_2CH_2NCH_2P$), 2.80 (m, 32 H, CH_2NCH_2P), 3.54 (m, 64 H, NCH_2P), 7.20 (m, 192 H, phenyl), 7.37 (m, 128 H, phenyl). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 23.99 (s, C*10*), 24.26 (s, C*4*/*7*), 24.70 (s, C*1*), 51.77 (s, C*9*), 51.97 (s, C*8*), 52.47 (s, C*5*/*6*), 52.68 (s, C*3*), 54.67 (t, $^3J(C,P)$ = 9.5 Hz, C*11*), 58.78 (dd, $^1J(C,P)$ = 14.1 Hz, $^3J(C,P)$ = 8.6 Hz, NCH_2P), 128.29 (m, phenyl), 133.03 (d, $J(C,P)$ = 18.2 Hz, phenyl), 138.28 (d, $J(C,P)$ = 13.3 Hz, phenyl). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = −28.01 (s); elemental analysis calcd. for $C_{504}H_{560}N_{30}P_{32}$: C 75.39, H 7.03, N 5.23, P 12.34; found: C 75.18, H 6.91, N 5.24, P 12.59.

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Keywords: homogeneous catalysis · dendrimers · Heck reaction · hydroformylation · palladium · rhodium

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[3] A silane-dendrimer having 12 arylnickel(II)-bearing endgroups, a compound which catalyzes the addition of CCl_4 to methyl methacrylate in a Kharasch reaction, has been described; however, separation from the product and recyclability of the catalyst are not mentioned: J. W. J. Knapen, A. W. van der Made, J. C. de Wilde, P. W. N. M. van Leeuwen, P. Wijkens, D. M. Grove, G. van Koten, *Nature* **1994**, *372*, 659.

[4] A dendrimer with six TADDOL endgroups has been prepared and the corresponding Ti alkoxides function as catalysts (20 mol%) in the addition of Et_2Zn to benzaldehyde; separation of the metal-free ligand following aqueous workup was accomplished by column chromatography: D. Seebach, R. E. Marti, T. Hintermann, *Helv. Chim. Acta* **1996**, *79*, 1710.

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[9] Designation of **2** according to the Newkome nomenclature [1]: 32-cascade:1,4-diaminobutane[4]:(1-azabutylidene)^3:diphenylphosphinomethane).

[10] Mass spectrometric methods such as matrix-assisted time-of-flight mass spectrometry (MALDI-TOF-MS) or electrospray mass spectrometry (ESI-MS) were not successful for the phosphinomethylated dendrimers **2** or for the corresponding metal complexes **3**–**6**.

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[12] Mechanistically it can be assumed that the Pd complex **4** as precatalyst undergoes a thermally induced, ethane-producing reductive elimination with formation of the corresponding 14-electron chelate [16]. This adds oxidatively to bromobenzene **9**, thereby initiating the Heck reaction. On completion of the reaction, the ^{31}P NMR spectrum of the separated solid material in [D$_8$]DMF shows a single signal at $\delta = +23$ as a sharp singlet. It is possibly an anionic Pd species [17].

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Isolation of the Quinone Mono *O,S*-Acetal Intermediates of the Aromatic Pummerer-Type Rearrangement of *p*-Sulfinylphenols with 1-Ethoxyvinyl Esters**

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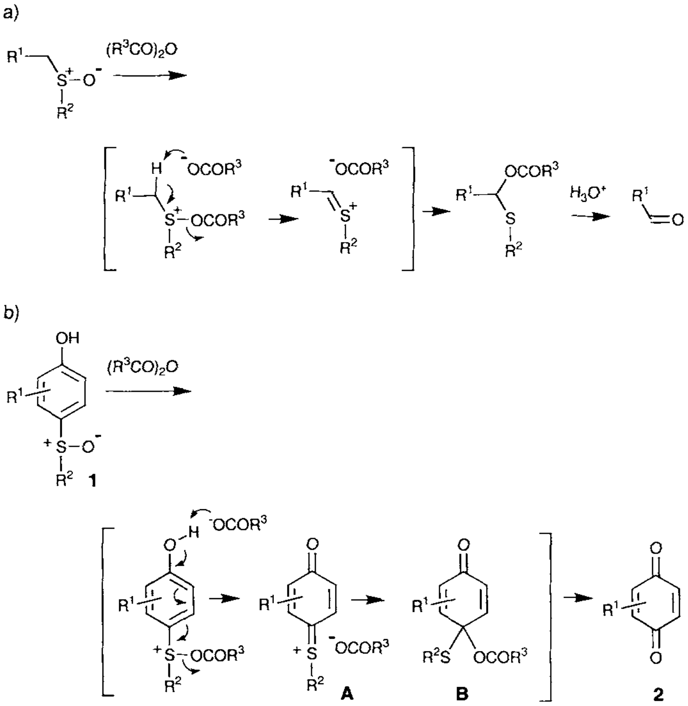
Treatment of aliphatic sulfoxides with acid anhydrides leads to a Pummerer rearrangement to give *O,S*-acetals. Because these products can be readily hydrolyzed to carbonyl compounds, these reactions have been widely utilized in a variety of organic syntheses (Scheme 1 a).[1] On the other hand, similar reactions of aromatic sulfoxides have not been extensively explored. Pummerer-type rearrangements of *p*-sulfinylphenols **1** would be an effective method for the preparation of *p*-quinones **2** via the *O,S*-acetals **B** and would also be interesting from a mechanistic standpoint (Scheme 1 b). King and Jung et al. have reported related studies on the reaction of acid anhydrides with 3,5-dimethyl-4-(methylsulfinyl)phenol[2] and with 4-methyl-2-(arylsulfinyl)phenols.[3, 4] The main products in these reactions were obtained through conjugate addition of nucleophiles to the sulfonium ions (like **A**), while the *O,S*-acetals (like **B**) were obtained in very low yield[2] and only in very few cases.[4]

At the same time as the publications by Jung et al.,[3, 4] we reported the Pummerer-type rearrangement of fully substituted *p*-sulfinylphenols **1** using trifluoroacetic anhydride (TFAA) as an effective method for preparation of *p*-quinones **2**.[5] We then extended this method to the *o*-unsubstituted *p*-sulfinylphenols **1** using TFAA and allyltrimethylsilane[6] and also to the silyl ethers of **1**, which enabled us to carry out the selective preparation of dihydroquinones.[7] Our results are noteworthy because they show novel *ipso*-substitution of sulfur functional groups into oxygen functional groups on phenol rings.



Scheme 1. a) Pummerer rearangement of aliphatic sulfoxides; b) Pummerer-type rearrangement of aromatic sulfoxides.

Although all of these reactions are certainly thought to proceed via the quinone mono *O,S*-acetals **B**, we were never able to isolate or even identify such acetal intermediates by spectroscopy. Difficulties in isolating **B** have been described previously[2–4] are probably due to the use of acid anhydrides as the initiator because acids or counteranions generated from the reagents would readily react with **B**.

Isolation of the acetal **B** is attractive from the view point of the utility of these compounds as useful synthons as well as the support of our proposed reaction mechanism. Here, we report the first isolation of the *O,S*-acetals **3** by employing 1-ethoxyvinyl esters **2a,b** for the Pummerer-type rearrangement of *p*-sulfinylphenols **1**.[8, 9] Selective transformation of **3** into the quinones **4** and the dihydroquinone **6** was also achieved. This success is attributed to the fact that the reactions with the ketene acetal reagents **2**[10] can be carried out under nearly neutral conditions, thereby releasing neutral and stable ethyl acetate as a single side product.

We initially examined the Pummerer-type reaction of tetramethyl-4-(phenylsulfinyl)phenol (**1a**) using 1-ethoxyvinyl acetate (**2a**) (5 equiv) under various conditions. The reaction in dry MeCN or dry toluene without a catalyst proceeded very slowly and required a high temperature or a long reaction time, resulting in the formation of several products but not the *O,S*-acetal **3a**. On the other hand, use of a catalytic amount of *p*-toluenesulfonic acid (*p*-TsOH) in dry toluene sufficiently accelerated the reaction, so that **3a** could be isolated in 69% yield after stirring at 60 °C for 1 h (Table 1). This result is completely different from that obtained by a similar treatment of **1a** with acetic anhydride and a catalytic amount of *p*-TsOH in toluene at refluxing temperature: this reaction afforded the corresponding

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