[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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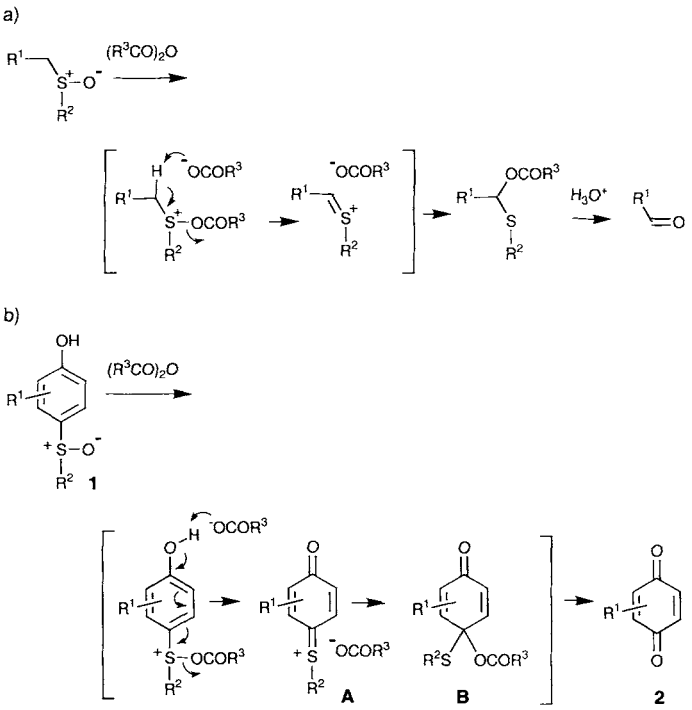

Scheme 1. a) Pummerer rearrangement of aliphatic sulfoxides; b) Pummerer-type rearrangement of aromatic sulfoxides.

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

Yasuyuki Kita,* Yoshifumi Takeda, Masato Matsugi, Kiyosei Iio, Kentoku Gotanda, Kenji Murata, and Shuji Akai

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 1a).[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 1b). 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.

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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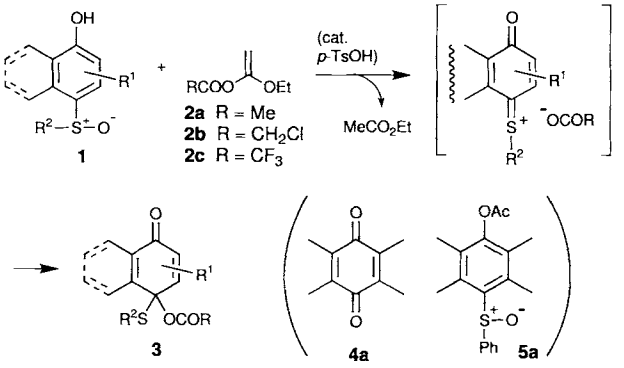
[**] This research was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan and Special Coordination Funds of the Science and Technology Agency, Japan.

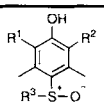
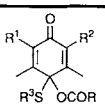
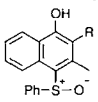
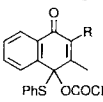
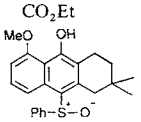
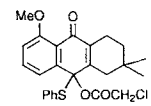
acetate **5a** quantitatively, which did not react further with **2a**. Use of the chloroacetate **2b** instead of **2a** gave the acetal **3b** in 81% yield. In contrast, the more reactive trifluoroacetate **2c** did not give the *O,S*-acetal **3** but the benzoquinone **4a** (40% yield). The reactions with 1-ethoxyvinyl benzoate (R = Ph) and the *p*-nitrobenzoate (R = *p*-$NO_2C_6H_4$) were slow and gave low yields of **4a** (Scheme 2). Thus, the chloroacetate **2b** was found to be a suitable reagent for preparation of the *O,S*-acetal **3**.



Scheme 2. Reaction of the *p*-sulfinylphenol **1** with the 1-ethoxyvinyl esters **2a–c**.

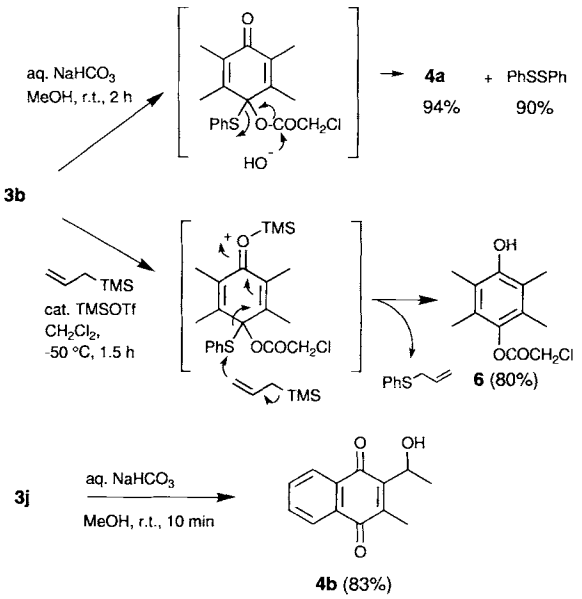
The reactions of various types of *p*-sulfinylphenols **1b–g** and naphthols **1h–j** with **2a,b** were carried out in an analogous manner to that applied for the preparation of **3a,b**, and the results are summarized in Table 1. The reactions were usually complete at room temperature or at 60 °C within several hours. Quenching the reaction mixture with Et_3N or K_2CO_3 followed by concentration and quick purification by chromatography on SiO_2 enabled us to isolate the products **3** in moderate to high yields. The compounds were identified by spectroscopy and can be stored under a nitrogen atmosphere in a refrigerator. Usually, **2b** provided **3** in higher yields. Both aliphatic and aromatic sulfinyl groups could be employed for this transformation. Allyl, ester, and hydroxyl groups are compatible with these reactions (entries 9–11). The formation of the *o*-unsubstituted products **3f,g** was also achieved in good yields (entries 6,7).

Table 1. Reactions of the *p*-sulfinylphenols **1a–j** with the 1-ethoxyvinyl esters **2a,b** to give the *O,S*-acetals **3a–l**[a].

Entry	1				2	T[°C]	t[h]	3		Yield[%]
										
		R^1	R^2	R^3					R	
1	**1a**	Me	Me	Ph	**2a**	60	1	**3a**	Me	69
2	**1a**	Me	Me	Ph	**2b**	60	1	**3b**	CH_2Cl	81
3	**1b**	Me	Me	Me	**2a**	20 → 60	9	**3c**	Me	86
4	**1b**	Me	Me	Me	**2b**	60	2	**3d**	CH_2Cl	80
5	**1c**	Me	Me	*t*Bu	**2b**	20	15	**3e**	CH_2Cl	74
6	**1d**	H	H	Ph	**2b**	60	2	**3f**	CH_2Cl	51
7	**1e**	Me	H	Ph	**2b**	20	2	**3g**	CH_2Cl	65
8	**1f**	Me	Et	Ph	**2b**	20	4	**3h**	CH_2Cl	81
9	**1g**	Me	allyl	Ph	**2b**	60	1	**3i**	CH_2Cl	77
										
		R								
10	**1h**	CH(OH)Me			**2b**	60	1	**3j**		80[b]
11	**1i**	CO_2Et			**2b**	20	24	**3k**		84
										
12	**1j**				**2b**	60	3	**3l**		71

[a] *p*-TsOH (0.01–0.05 equiv) in toluene. For a typical procedure see the *Experimental Section*. [b] Obtained as a 1:1 mixture of two diastereomers.

Treatment of **3b** with aqueous $NaHCO_3$ in MeOH at room temperature caused selective saponification of the chloroacetate and the concomitant elimination of the phenylthio group to give the corresponding quinone **4a** and the disulfide PhSSPh in 94 and 90% yield, respectively. On the other hand, **3b** reacted with allyltrimethylsilane in the presence of a catalytic amount of trimethylsilyl trifluoromethanesulfonate (TMSOTf) to afford an 80% yield of the dihydroquinone **6** and allyl phenyl sulfide. Mild alkaline treatment of **3j** led to the rapid formation of quinone **4b** in 83% yield (Scheme 3). Thus, selective conversion



Scheme 3. Conversion of the *O,S*-acetals **3b** and **3j** to the quinones **4a** and **4b** and the dihydroquinone **6**.

of **3** to both quinones and dihydroquinones was achieved by the choice of the reaction conditions, which also supports the reaction mechanism for our previously reported preparation of quinones and dihydroquinones from *p*-sulfinylphenol derivatives.[5–7]

The present results are of particular interest from the view point of the direct preparation of quinone monoacetals from aromatic compounds under *nonoxidative* conditions.[11] Extended studies on the utilization of the products **3** as versatile synthons are now under investigation.

Experimental Section

Typical procedure for the reaction of the *p*-sulfinylphenol **1** and 1-ethoxyvinyl esters **2a,b**: Under a nitrogen atmosphere, **2b** (0.82 g, 5.0 mmol) [9c, 10] and anhydrous *p*-toluenesulfonic acid (9 mg, 0.05 mmol) were successively added to a suspension of the *p*-sulfinylphenol **1a** (0.27 g, 1.0 mmol) in dry toluene (30 mL). The reaction mixture was stirred at 60 °C for 1 h and cooled to room temperature. Triethylamine (0.007 mL) was added and the reaction mixture was concentrated in vacuo. The residue was purified by SiO_2-flash column chromatography (hexane/ethyl acetate 8/1) to give the quinone mono *O,S*-acetal **3b**: pale yellow crystals (yield 81%); m.p. 132–133 °C (hexane/ethyl acetate); IR (KBr): $\tilde{\nu}$ = 1776, 1662, 1630 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ = 1.64 (s, 6H), 2.01 (s, 6H), 4.16 (s, 2H), 7.01 (d,

$J = 7.5$ Hz, 2H), 7.21 (t, $J = 7.5$ Hz, 2H), 7.38 (t, $J = 7.5$ Hz, 1 H); MS (EI, 70 eV): m/z (%): 352 (0.6) [$M^+ + 2$], 350 (1.6) [M^+], 165 (100), 110 (57); HRMS calcd for $C_{18}H_{19}{}^{35}ClO_3S$ (M): 350.0742, found: 350.0727; elemental analysis: calcd C 61.62, H 5.46; found: C 61.61, H 5.32.

Received: January 3, 1997 [Z9959IE]
German version: *Angew. Chem.* **1997**, *109*, 1525–1527

Keywords: acetals · Pummerer rearrangement · quinones · rearrangements · sulfur

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[8] We have elucidated a highly enantioselective Pummerer-type reaction of chiral, nonracemic aliphatic sulfoxides using *O*-silylated ketene acetals [1d], although the enantiomeric excesses for the reported asymmetric Pummerer reaction induced by acid anhydrides were low [1]. This method was efficiently applied to the asymmetric Pummerer-type cyclization of chiral, nonracemic sulfoxides and to the biomimetic conversion of Arnstein tripeptide analogs into optically active *cis* β-lactams. This synthesis resembles penicillin biosynthesis [9a]. Similar highly enantioselective Pummerer-type reactions of chiral, nonracemic aliphatic sulfoxides induced by a variety of 1-ethoxyvinyl esters including **2a,b** also gave α-acyloxy sulfides [9b,c].

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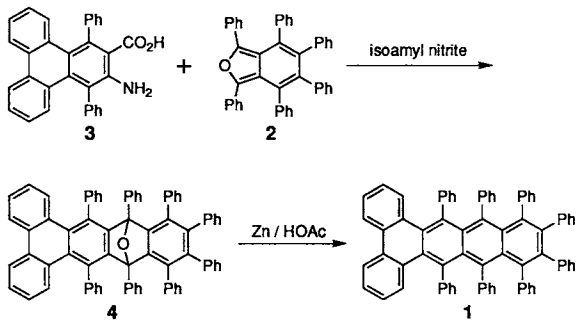
An Extraordinarily Twisted Polycyclic Aromatic Hydrocarbon**

Xiaoxin Qiao, Douglas M. Ho, and Robert A. Pascal, Jr.*

Among the most aesthetically pleasing chemical structures are polycyclic aromatic hydrocarbons (PAHs) that exhibit helical distortions from planarity.[1] In recent years a variety of longitudinally twisted PAHs and PAH derivatives—essentially twisted aromatic ribbons—have been prepared by the substitution of normally planar PAHs with bulky substituents.[2, 3] Thus, for example, anthracene is a planar molecule, but decaphenylanthracene exhibits an end-to-end twist of 63°.[3] In no case, however, has the overall twist of such a molecule exceeded 70°,[4] and we wondered what would be the properties of a PAH in which the twist exceeded 90°. We now report the synthesis and crystallographic characterization of 9,10,11,12,13,14,15,16-octaphenyldibenzo[*a*,*c*]naphthacene (**1**), a PAH with an extraordinary end-to-end twist of 105°.

The synthesis of **1** is similar to that of decaphenylanthracene;[3] the critical step is the addition of a highly substituted aryne to hexaphenylisobenzofuran[3, 5] (**2**) (Scheme 1). Thus,



Scheme 1.

the anthranilic acid **3**[2d] was diazotized in the presence of **2**, and the resulting oxide **4** was deoxygenated with zinc in acetic acid to yield compound **1** in 1.6% overall yield. Both the cycloaddition of the aryne with isobenzofuran (15% yield) and the deoxygenation (11%) suffer from severe steric hindrance, which accounts for the low yield in an otherwise simple procedure.

Compound **1** is an orange solid that is readily soluble in a wide variety of organic solvents, in contrast with many PAHs. Orange prisms were obtained from ethanol, and X-ray structure analysis unambiguously established the structure of **1** (Figure 1).[6] The molecule lies on a crystallographic C_2 axis, thus its site symmetry is equal to its expected molecular symmetry. The central naphthacene moiety is a smoothly twisted aromatic ribbon in which the terminal bonds [C(1)–C(1′) and C(13)-C(13′)] are rotated by 105.4(8)° with respect to each other. However, the distortion is evenly distributed among the four benzene rings of the naphthacene, which contribute twists of 26.1(8)°, 28.7(8)°, 28.6(8)°, and 21.9(8)°, thus enabling good conjugation to be maintained within the aromatic π system. Indeed, the UV spectrum of **1**, with absorption maxima at 496, 470, and 364 nm, retains most of the features found in the spectrum of the parent hydrocarbon, dibenzo[*a*,*c*]naphthacene,[9] but shifted by about 50 nm to the red.

Compound **1** is very stable in the solid state. Crystals heated to 400 °C in an open capillary appear unchanged (apart from some cracking) by visual inspection and mass spectrometric and thin-layer chromatograpic analyses. Concentrated solutions of **1** appear to undergo slow decomposition at room temperature, but the factors governing this process are unclear. However, a dilute solution of **1** (1.8×10^{-5} M in dimethyl sulfoxide), monitored spectrophotometrically, was indefinitely stable at 50 °C even in the presence of air and added HCl, and an NMR sample (1.6×10^{-3} M in $CDCl_3$) showed no decomposition after one week at room temperature.

The preparation of **1** establishes a new record for the twisting of an aromatic π-electron system, and its end-to-end twist of

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[**] This work was supported by the National Science Foundation (grant CHE-9408295).

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