the 1-naphthyl-4-quinoline *S*-**3** (87%). The latter, on HPLC (reverse phase, 8.2:1 MeOH–H_2O) gave an 84:16 ratio of diastereomers indicating that the oxidation proceeded with virtually complete conservation of chirality albeit in the presence of the chiral oxazoline. When the process was repeated using **1** and naphthylmagnesium bromide, the epimeric dihydroquinoline **4** was the major product as determined by HPLC analysis of the urethane **4a**. The ratio of **4a**:**2a** was 86:14. Oxidation of **4** with DDQ (THF, −78 °C) gave the biaryl **5** (80%) whose diastereoisomeric composition was assessed (HPLC) as 88:12 ± 1% indicating once again that **5** was formed with virtually complete conservation of chirality (Scheme I). Thus, a synthesis enriched in either diastereomer was in hand, and each was oxidized with virtually complete destruction of the stereochemistry at C-4 and the creation of the axial chiral element in **3** and **5**, respectively. An X-ray structure determination was performed on the pure *t*-Boc derivative of **4**[12] after removal of the contaminating epimer **2** by radial chromatography (EtOAC–hexane) and then crystallization (CH_2Cl_2–pentane). HPLC analysis confirmed the total purity of **4** (R = *t*-Boc) and complete absence of **2**.

The X-ray structure of **4** indicates that the absolute configuration of the newly created chiral element is *R*. Since the *R* center in **4** came from Grignard addition, the *S* center in **2** undoubtedly arose from naphthyllithium addition. An X-ray structure determination was also performed on the biaryl **5**,[13] which was purified from its epimer **3** by chromatography and crystallization as above. The configuration due to the axial chiral element in **5** was shown to be *R* (Figure 1).[14] The oxazoline was removed from **5** by hydrolysis (6M H_2SO_4, reflux) to the carboxylic acid and immediately transformed into the methyl ester *R*-**5a** [mp 101–102.5 °C, $[\alpha]_D$ +13.16° (*c* 1.1, $CHCl_3$)].

The oxidation of **4** to **5** with complete conservation of chirality raised a concern over whether the naphthalene addition to **1** gave rise to *two* elements of chirality and oxidation merely removed the chirality element at C-4, leaving the naphthalene ring in the observed configuration. This concern arises if there is hindered rotation of the naphthalene ring in **2** and **4**. However, NMR studies at temperatures between +45 and −80 °C indicate clearly that the barrier to naphthalene rotation is below 18 kcal and therefore it is free to rotate[15] in agreement with other studies on 9-arylxanthyls,[16a] 9-arylthioxanthyl,[16b] and 9-arylfluorenes.[17] Furthermore, oxidation of **2** or **4** gave identical ratios of **3** and **5** at all temperatures in the range of −78 to +40 °C. This is strong support that, although naphthalene rotation is occurring, access to the hydrogen at C-4 in *R*-**4** is only possible when the nonconnective benzene ring is as far as possible from the hydride to be removed, thus leading to *R*-**5**. The previous results may be considered adequate proof of the Berson postulate for central to axial transfer by conversion of *S*-**2** to *S*-**3** (or *R*-**4** to *R*-**5**). However, the presence of the oxazoline in **2** and **4** could have been responsible for the efficient transfer observed. It was therefore critical to see if this process could be repeated in the absence of any chiral element other than that which is destroyed or created during the oxidation.

The oxazoline in **2a** (88:12 diastereomeric mixture, ±1%) was removed ($MeOSO_2F$, CH_2Cl_2; $NaBH_4$, MeOH–THF; oxalic acid–silica gel) to the aldehyde *S*-**6** in 96% yield ($[\alpha]_D$ +149.6°, $CHCl_3$) and transformed to the aldehydo dihydroquinoline *S*-**6a** (KOH–H_2O–THF–EtOH). Due to the tendency of **6a** to deteriorate on standing, it was directly oxidized (DDQ, −78 to 25 °C) to the biaryl aldehyde *S*-**7** in 90% yield ($[\alpha]_D$ −93.3°, $CHCl_3$). In order to assess the enantiomeric purity of *S*-**7** and the efficiency of the transfer, the aldehyde was oxidized (90%) and esterified (98%) to the ester, *S*-**7a**, already prepared pure and with known absolute configuration. To our delight *S*-**7a** showed $[\alpha]_D$−10.60° ($CHCl_3$), which corresponds to a 90:10 ±1% enantiomeric ratio in good agreement with the 88:12 ratio in **2a**. This confirmed that the stereochemical transfer from C-4 to the biaryl in the absence of any external chiral elements was virtually complete. It may, therefore, be concluded that the DDQ oxidation occurred in a manner that precluded any racemization (Figure 1) and verified the Berson prediction. Studies to utilize these chiral substances as reagents for asymmetric syntheses are in progress.

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Supplementary Material Available: X-ray structures and data along with spectral properties of **1**–**7** (12 pages). Ordering information is given on any current masthead page.

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(12) **4** (R = *t*-Boc): mp 148.5–151.5 °C, $[\alpha]_D$ −91.4° (*c* 1.1, $CHCl_3$). Anal. C, H. X-ray details are given as supplementary material.

(13) **5**: mp 203–206 °C, $[\alpha]_D$ −51.26° (*c* 1.1, $CHCl_3$). Anal. C, H. X-ray details are given as supplementary material.

(14) The scheme in Figure 1 is shown for the *R* enantiomers, taken from the X-ray structures for these same substances.

(15) Additional support for naphthalene rotation in the aldehyde **6a** prior to oxidation to **7** was gathered by use of the 7′-methoxy derivative of **6a**. Only a single 7′-methoxy and a single C-4 proton in the quinoline were observed in the ^1H NMR at temperatures down to −50 °C. Below this (−60 to −75 °C) both signals separated into the two conformers.

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Modification of the Free-Radical Thermolysis of Bibenzyl by Surface Immobilization[1,2]

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We report initial observations concerning thermolysis of 1,2-diphenylethane immobilized on a silica surface. Although there have been studies of decomposition of free-radical precursors physisorbed on silica gel,[4] we are not aware of studies in which the precursor was covalently attached. We present evidence that *surface immobilization can lead to enhancement of unimolecular radical decay pathways relative to bimolecular ones.*

Determination of the mechanisms of thermolysis of α,ω-diphenylalkanes, $Ph(CH_2)_nPh$, in the fluid state has been stimulated recently[3,5-7] because they serve as models of reactive sites during thermal conversions of coal.[8] However, initially formed reactive

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intermediates in coal will remain covalently attached to the cross-linked macromolecular framework;[9] hence their reactivity may be subject to diffusional restraints. We are exploring this complication by studies of thermolysis of model compounds immobilized on inert solids.

Reaction of phenols **1** with fumed silica[10] at 200–250 °C followed by evacuation at 300 °C gave the desired surface-attached starting materials **2**.[11] Surface-attached species were liberated

$$\equiv\mathrm{SiOH} + \underset{\mathbf{1}}{p\text{-}\mathrm{HOC_6H_4(CH_2)}_n\mathrm{C_6H_5}} \rightarrow \underset{\mathbf{2}}{\equiv\mathrm{SiOC_6H_4(CH_2)}_n\mathrm{C_6H_5}} + \mathrm{H_2O}$$

$$\mathbf{a},\ n = 0;\ \mathbf{b},\ n = 1;\ \mathbf{c},\ n = 2$$

for analysis as phenols by dissolution of the sample in aqueous base. Typical coverage was 0.5 mmol $\mathrm{g^{-1}}$ (1.5 $\mathrm{nm^{-2}}$). Although the surface density of hydroxyl groups on amorphous silica[12] is somewhat higher ($\sim$5 $\mathrm{nm^{-2}}$), steric considerations suggest that such coverage approaches a two-dimensional film. Thermolyses were carried out in evacuated, sealed, Pyrex tubes with the heated end containing solid **2** ($\sim$0.13 g $\mathrm{mL^{-1}}$) and the other end held at 77 K to collect volatile products as formed. Volatile and surface-attached products were analyzed separately by GC and GC/MS.

The only chemical change detected when surface-attached biphenyl **2a** was heated at 400 °C for 4 h was evolution of 13% of phenol **1a**.[13] Homologue **2b** behaved analogously.[14] In contrast, thermolysis of **2c** gave complex mixtures of both volatile and surface-attached products. For a typical run of 2.5 h, 13.0 mol % of the surface-attached bibenzyl units were evolved as phenol **1c** and 63.6 mol % were recovered unchanged. The 14 products listed below accounted for a 94% carbon material balance of the remainder. Hence no *major* products appear to remain undetected. As a preliminary estimation of primary products, data at 0.5–4.0 h were extrapolated linearly to zero time to give the following product distribution (mol %): $\equiv\mathrm{SiOC_6H_4CH(C_6H_5)CH_3}$ (**3**, 52.9);[15a] $\equiv\mathrm{SiOC_6H_4CH_3}$ (**4**, 9.5); $\mathrm{C_6H_5CH_3}$ (**5**, 6.6); $\equiv$SiO-3-phenanthryl (**6**, 5.4);[15b] $\equiv\mathrm{SiOC_6H_5}$ (**7**, 4.2); $\equiv\mathrm{SiOC_6H_4CH{=}CHC_6H_5}$ (**8**, 3.9); $\equiv\mathrm{SiOC_6H_4CH_2CH_3}$ (**9**, 3.5); $\mathrm{C_6H_5CH_2CH_3}$ (**10**, 2.2); $\mathrm{C_6H_6}$ (**11**, 2.0); $\equiv\mathrm{SiOC_6H_4CH_2C_6H_5}$ (2.0); $\mathrm{C_6H_5CH{=}CH_2}$ (**12**, 1.7); $\equiv\mathrm{SiOC_{14}H_{11}}$ isomer (1.7); $\mathrm{C_6H_5CH_2CH_2C_6H_5}$ (**13**, 1.3); $\equiv\mathrm{SiOC_{14}H_9}$ isomer (0.9).

The initial liquid-phase products are quite different: **5**, $\mathrm{C_6H_5CH_2CH(C_6H_5)CH(C_6H_5)CH_2C_6H_5}$, $\mathrm{C_6H_5CH{=}CHC_6H_5}$, $\mathrm{(C_6H_5)_2CHCH_3}$ (**14**), and $\mathrm{C_6H_5CH_2CH(C_6H_5)CH_2C_6H_5}$ in a molar ratio of 56:21:10:10:2 with only traces of **10**, **11**, and phenanthrene.[5,6a] In the fluid state,[5,6a] rate-controlling homolysis gives two benzyl radicals (**15**) which largely abstract hydrogen from starting material **13** to form **5** and 1,2-diphenylethyl radical (**16**). The majority of **16** disappear by coupling–disproportionation. A minority lead to isomerized product **14** by reversible 1,2-phenyl shift followed by rate-limiting hydrogen abstraction. Although the isomerization pathway constitutes a radical-induced chain, its chain length (defined as **14**/(**5**/2)) is only $\sim$0.35 in the neat liquid and decreases even further with increasing dilution. Finally, a miniscule fraction of radical **16** may lead to phenanthrene by a not yet understood[6a] cyclization–dehydrogenation pathway.

We do not yet understand all the mechanistic modifications associated with surface attachment, but we make the following observations and working hypotheses:

(1) The formation of both free and surface-attached $\mathrm{C_7}$ products suggests that C–C homolysis (eq 1) remains the initial event. On

$$\underset{\mathbf{2c}}{\equiv\mathrm{SiOC_6H_4CH_2CH_2C_6H_5}} \rightarrow \underset{\mathbf{17}}{\equiv\mathrm{SiOC_6H_4CH_2}\cdot} + \underset{\mathbf{15}}{\cdot\mathrm{CH_2C_6H_5}} \tag{1}$$

the basis of (**4** + **5** + 2(**13**)), we estimate $k_1 \sim 7 \times 10^{-6}\ \mathrm{s^{-1}}$. Reported values[6b] for the corresponding homogeneous process at 400 °C are $10.3 \times 10^{-6}\ \mathrm{s^{-1}}$ (gas phase) and $7.6 \times 10^{-6}\ \mathrm{s^{-1}}$ (tetralin solution). Thus surface attachment has had minimal effect on the initial bond scission.

(2) The comparable amounts of products from free and surface-attached $\mathrm{C_7}$ radicals [(**5** + 2(**13**))/(**4**) = 0.97] suggest that there is enough conformational mobility at the high surface coverages employed herein to allow surface-attached radical **17** to abstract hydrogen from an adjacent **2c** unit (eq 2).[16,17]

$$\mathbf{17} + \mathbf{2c} \rightarrow \underset{\mathbf{4}}{\equiv\mathrm{SiOC_6H_4CH_3}} + \underset{\mathbf{18}}{\equiv\mathrm{SiOC_6H_4\dot{C}HCH_2C_6H_5}} \tag{2}$$

$$\mathbf{15} + \mathbf{2c} \rightarrow \underset{\mathbf{5}}{\mathrm{C_6H_5CH_3}} + \mathbf{18} \tag{3}$$

(3) The dominant product change accompanying surface attachment is the dramatic increase in the rearrangement process. Thus the chain length of the rearrangement sequence (eq 4) has

$$\mathbf{18} \rightleftarrows \equiv\mathrm{SiOC_6H_4CH(C_6H_5)CH_2}\cdot \xrightarrow[-\mathbf{18}]{+\mathbf{2c}} \underset{\mathbf{3}}{\equiv\mathrm{SiOC_6H_4CH(C_6H_5)CH_3}} \tag{4}$$

increased to >5.5. We suggest that bimolecular radical–radical decay pathways for **18** have been inhibited by surface immobilization, and therefore decay pathways that are first order in radicals are effectively enhanced.

(4) The second major product change is the emergence of cyclization–dehydrogenation to form surface-attached phenanthrene (**6**) and of aromatic dealkylation to form $\mathrm{C_6}$ and $\mathrm{C_8}$ products (**7**, **9**, **10**, **11**, and **12**) from relative obscurity to stoichiometric significance. We refrain from further mechanistic speculation except to note that (1) the enhanced cyclization of radical **18** to a tricyclic structure is again probably a unimolecular decay pathway and (2) the dealkylation pathway may be diagnostic of hydrogen atoms[18] generated at some point between **18** and **6**.[19]

In the context of coal conversion both the cyclization–dehydrogenation and the rearrangement pathways are undesirable because they produce a structure more refractory than the starting material. In a broader context, we are considering the possibility that surface immobilization may be a rather general procedure to allow observation of unimolecular transformations of reactive species that are normally overwhelmed in fluid media by encounter-controlled bimolecular decay pathways.

Registry No. **1** (n = 0), 92-69-3; **1** (n = 1), 101-53-1; **1** (n = 2), 6335-83-7; bibenzyl, 103-29-7.

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[16] Species **18** is presumably a mixture of $\equiv\mathrm{SiOC_6H_4CH_2\dot{C}HC_6H_5}$ and the isomer shown.

[17] To satisfy stoichiometry the "added hydrogen" atom in **4** and **5** must be derived partly from hydrogen abstraction from **2c** and partly from disproportionation routes leading to **6** and **8**.

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