Bimolecular Formation of Radicals by Hydrogen Transfer, 15[+]

New Hydrogen Transfer Catalysts

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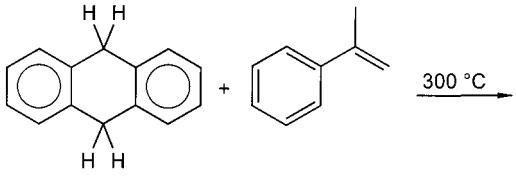
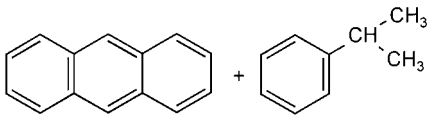
The transfer of hydrogen from excess 9,10-dihydroanthracene (DHA) to acceptors such as α-methylstyrene is catalyzed, i.e. occurs at temperatures in the range 200–260 °C instead of 280–320 °C, when hydrocarbons with weaker C–H bonds than DHA, e.g. 6*H*-benzo[*cd*]pyrene (**4**), 7*H*-dibenzo[*a*,*kl*]anthracene (**5**), 4-methyl-7*H*-benzo[*de*]naphthacene (**6**) or 8*H*-dibenzo[*b*,*fg*]pyrene (**7**), are added to the reaction mixture. The reactions are initiated by bimolecular H-atom transfer from **4**–**7** to the acceptor (retrodisproportionation) and proceed by nonchain radical mechanisms. This is supported by isotopic labelling and kinetic isotope effects, substituent and solvent effects, EPR spectroscopy of intermediate radicals, and by a comparison of the thermochemical and kinetic characteristics of these reactions.

Introduction

In 1992, Rüchardt, Gerst and Nölke[1] reported the transfer hydrogenation of α-methylstyrene **1** by an excess of 9,10-dihydroanthracene (DHA) in diphenyl ether at 270−320°C, which furnished cumene and anthracene in almost quantitative yield.



DHA **1**



In a thorough mechanistic investigation,[2] this new reaction type was shown to proceed by a stepwise nonchain radical mechanism. It was later found that this new type of hydrogen transfer mechanism must be general to a broad range of hydrogen donors[2] (e.g. dihydronaphthalene, fluorene, xanthene,[3] 9,10-dihydroacridine,[3] alkyldihydronicotinamide,[4] etc.) and hydrogen acceptors[2] (e.g. styrenes,[5] dienes,[6] imines,[6b] azoarenes,[7] aromatic nitro and nitroso compounds,[7] and quinones[8]). The proposed general mechanism involves initiation by the transfer of a weakly bound hydrogen atom from the donor to the acceptor in a bimolecular *retrodisproportionation* step (1).

(1) A−H + B=C → A· + HB−C·
(2) HB−C· + A−H → HB−CH + A·
(3) 2 A· → disproportionation or dimerization

The adduct radical HB−C· is subsequently saturated by regular H transfer from the donor (2). Finally, the donor-derived radicals A· undergo disproportionation (e.g. for AH = DHA) or dimerization (e.g. for AH = xanthene). When an approximately *stoichiometric* amount of a hydrocarbon A′H possessing a much weaker C−H bond than DHA (see Table 1), e.g. phenalene **2**[2][9] or 7*H*-benz[*de*]-anthracene **3**,[2][10] was added to a mixture of excess DHA with **1**, a large increase in the reaction rate was observed. The concentration of **3** did not change during the hydrogen-transfer reaction,[10] whereas **2** was slowly hydrogenated to give dihydrophenalene since it possesses a double bond of the styrene type.[9] The "catalytic" action of the hydrocarbons A′H can be interpreted in terms of the following additional steps in the above mentioned mechanism:

(4) A′H + B=C → A′· + HB−C·
(5) A′H + HB=C· → A′· + HB−CH
(6) 2 A′· ⇌ A′−A′
(7) 2 A′· + 2 AH ⇌ 2 A′H + 2 A·
(8) 2 A· or A· + A′· → disproportionation

Only the radicals A· (derived form DHA) can be consumed by disproportionation, not those derived from **2** or **3** (A′H).

The aim of the present work is to extend the search for further catalysts A′H with a view to testing the hypothesis that their catalytic activity depends on their C−H bond energies. There is also interest in this "catalysis" phenomenon in the context of coal liquefaction technology.[11] Moreover,

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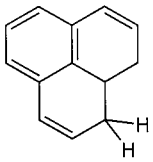
retrodisproportionation reactions [e.g. (1) and (4)] represent new radical initiator systems, e.g. for polymerization,[12] which merit further investigation. In order to make this initiation method practicable at lower temperatures, more effective H-transfer catalysts are required.[13][14]

The hydrocarbons 6*H*-benzo[*cd*]pyrene (**4**), 7*H*-dibenzo[*a,kl*]anthracene (**5**), 4-methyl-7*H*-benzo[*de*]naphthacene (**6**), 8*H*-dibenzo[*b,fg*]pyrene (**7**), and 4,5-methylenephenanthrene (**8**) were selected for studies of their reactivity as H-transfer agents and their effectiveness as catalysts of H-transfer by DHA, largely because of their ready availability. Furthermore, with the exception of **6**, they meet the requirement that the radicals generated upon H-abstraction cannot undergo disproportionation.[15] The bond energies of the reactive C−H bonds of **4**−**8** are given in Table 1.



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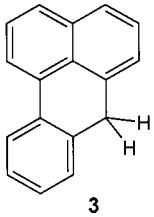

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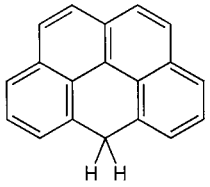

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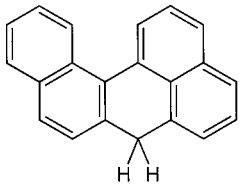

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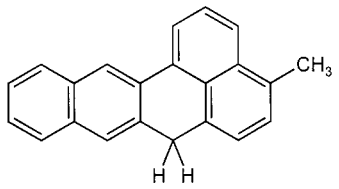

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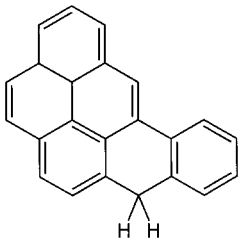

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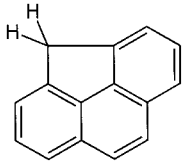

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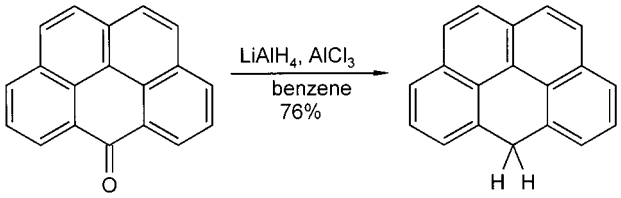
Synthesis

6*H*-Benzo[*cd*]pyrene (**4**) was prepared by first condensing glycerol with pyrene,[16] thereby generating 6*H*-benzo[*cd*]pyren-6-one. In contrast to a literature report, the ketone was obtained as a single isomer, as evidenced by its symmetrical ^{1}H-NMR spectrum. The ketone was reduced to **4** or [D_2]-**4** with $LiAlH_4$ and $LiAlD_4$, respectively, in the presence of $AlCl_3$.



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In a similar fashion, 7*H*-dibenzo[*a,kl*]anthracene **5** was prepared in excellent yield by $LiAlH_4/AlCl_3$ reduction of 7*H*-dibenzo[*a,kl*]anthrone **9b**. However, the synthesis of ketone **9b** proved to be more troublesome than might have been expected in the light of some literature reports.[17][18]

In our hands, the mixture of ketones **9a**−**9c** obtained by condensation of commercially available benz[*a*]anthracene-7,12-dione with aniline, glycerol, and sulfuric acid proved to be inseparable by chromatographic means. Pure **9b** was finally isolated from this mixture by fractional crystallization from large amounts of pyridine (16% yield). The melting point of **5** (167−168°C) was much higher than that reported previously (89.5−90.5°C)[19] for a sample prepared by a multi-step synthesis. This higher melting point compares more favorably with the melting points of other hydrocarbons of similar structure. The structures of **9b** and **5** have now been established on the basis of ^{1}H-NMR, ^{13}C-NMR, GC/MS and FT-IR data.

4-Methylbenzo[*de*]naphthacen-7-one **10** was prepared by oxidative ring-closure of 1-methylnaphthalene and 2-naphthoyl chloride in dry carbon disulfide using an excess of $AlCl_3$.[20] Besides the evidence provided by standard analytical methods (see Experimental Section), the structure was unequivocally established by X-ray analysis.

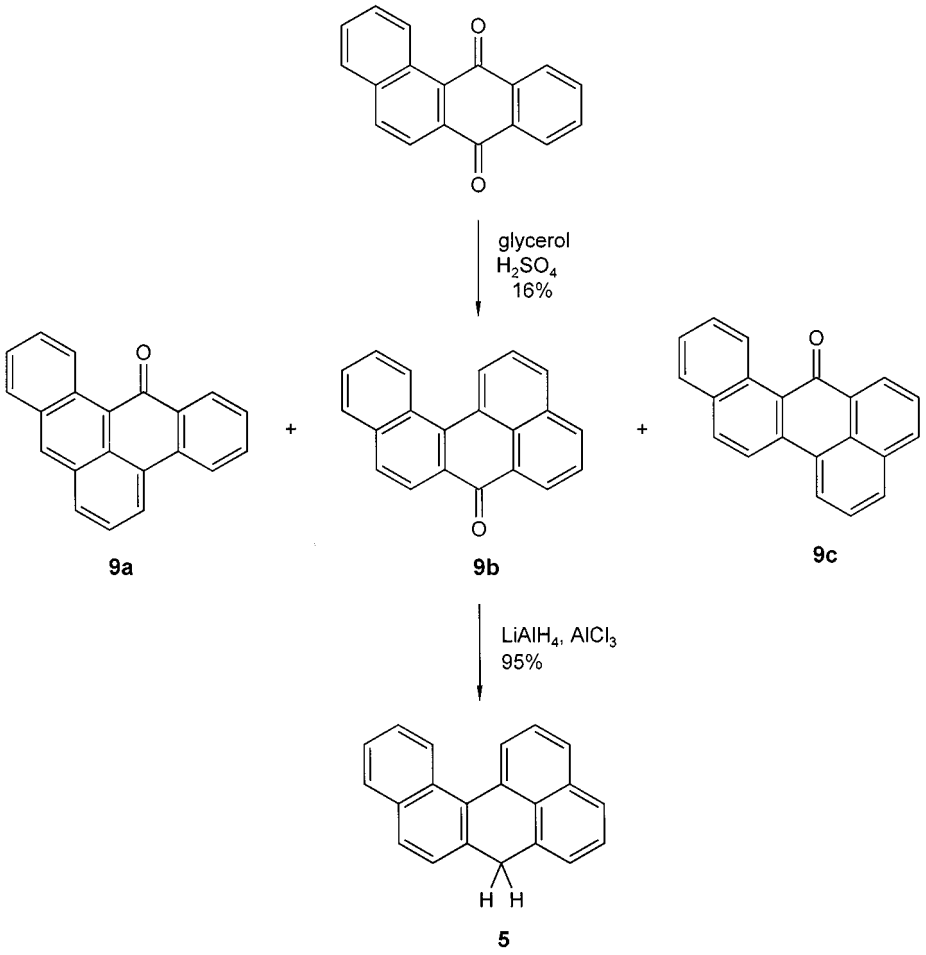
The ketone was reduced with $LiAlH_4$ and $AlCl_3$ in dry diethyl ether to yield 4-methyl-7*H*-benzo[*de*]naphthacene (**6**).

3-Benzoylpyrene was prepared by the addition of finely powdered aluminum chloride to a mixture of pyrene and benzoyl chloride, and was cyclized in an $AlCl_3$/NaCl melt to afford 8*H*-dibenzo[*b,fg*]pyren-8-one.[21] The yield of the latter was low due to the cumbersome purification procedures required. 8*H*-dibenzo[*b,fg*]pyrene (**7**) was obtained by reduction with $LiAlH_4$ and $AlCl_3$ in dry diethyl ether.

4,5-Methylenephenanthrene **8** is commercially available.

Results

The rates of H-transfer from the hydrocarbons **4**−**6** to α-methylstyrene (**1**) were measured as described previously for **2**[9] and **3**.[10] Typically, solutions of **1** (0.08 m), **4** (0.21 m), and DHA (1.00 m) in diphenyl ether were heated to 250°C and the product formation was monitored by gc. The presence of DHA, which does not transfer hydrogen to **1** at



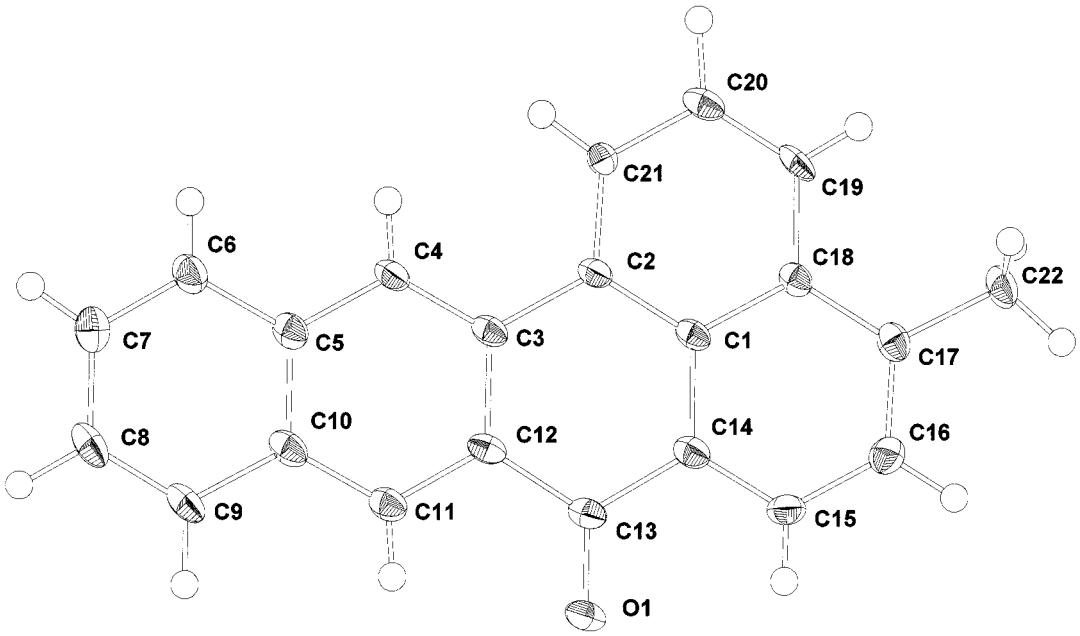
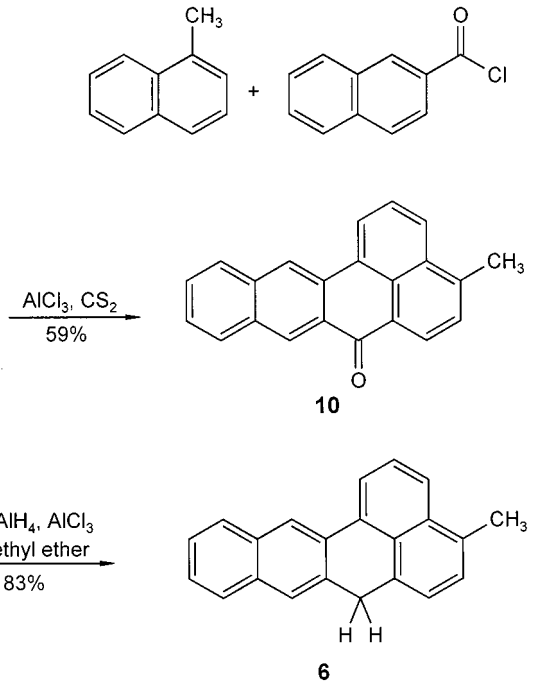


Figure 1. X-ray structure of 4-methylbenzo[*de*]naphthacen-7-one (**15**, for conditions of data collection, see Experimental Section)

this temperature, was necessary in order to obtain perfect product balances.[9][10] From Figure 2, it can be seen that the concentration of **1** decreases concomitantly with the increasing concentration of cumene and that the mass balance is quantitative. The concentration of the H-donor remains constant because of its continuous regeneration ac-



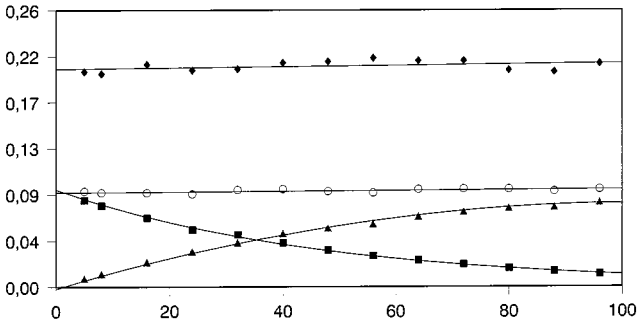


Figure 2. Mass balance of the transfer hydrogenation of **1** (0.08 M) with **4** (0.21 M) and DHA (1.00 M) in diphenyl ether at 250°C; filled square: **1**, filled triangle: cumene, circle: mass balance of **1** and cumene, rhomb: **4**

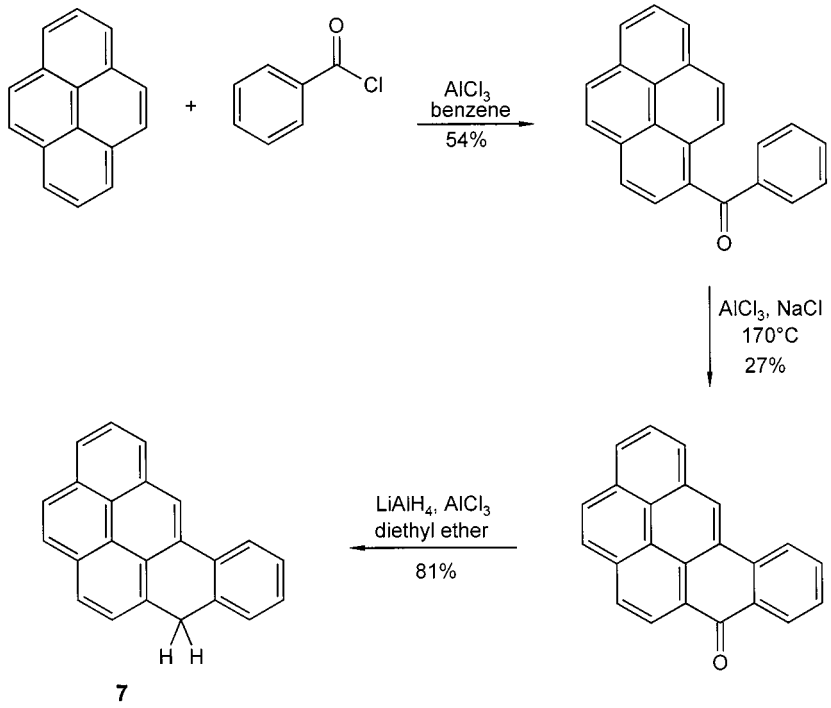
cording to reactions (7) and (8), which are fast processes due to the presence of an excess of DHA. We can thus refer to **4** as a "catalyst".

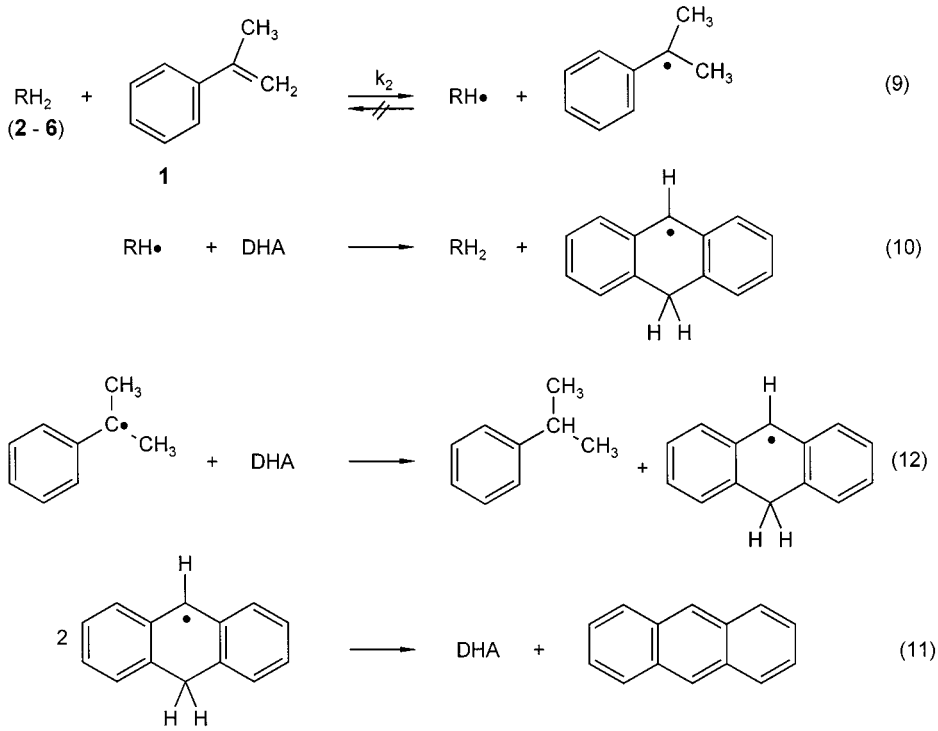
Plots similar to that depicted in Figure 2 were also obtained for **5** and **6**.[6b]

Hydrocarbon **7** proved to be insufficiently soluble to permit a quantitative investigation of its reactivity. Nevertheless, it could be established that 5% cumene and anthracene were formed when **7** (ca. 0.1 m) and **1** (0.05 m) were heated at 260°C with DHA (1.00 m) in diphenyl ether for 15 min. **8** reacted with **1** only at higher temperatures (330−370°C), at which DHA also reacts with **1**. Consequently, for the investigation of **8** as an H-donor, DHA was omitted and *sec*-butylbenzene was used both as a solvent and as a scavenger of the radicals derived from **2**. The mass balance of **1** and cumene was 85−95% under these conditions, but the concentration of **8** decreased by about 10% during the course of the reaction. As typical additional products derived from the solvent, α-ethylstyrene and 2-phenyl-2-butene were identified by gc.[22]

Under the aforementioned conditions, the consumption of **1** followed pseudo-first-order kinetics. By variation of the concentrations of the H-donors, first-order kinetics in **4** and **8** could also be set up.

The rate constants were measured over a temperature range of 40°C (220−260°C), allowing the activation parameters to be calculated using the Eyring equation.[22] These are presented in Table 1, together with previous results obtained for **2**, **3**, and DHA. The activation enthalpies $\Delta H^{\neq}$ of **2**−**6** decrease in line with their bond strengths,





Scheme 1

BDE (C−H), and the activation entropies $\Delta S^{\neq}$ are negative, having values between −26 to −30 cal K^{-1} mol^{-1} The unexpectedly small activation enthalpy $\Delta H^{\neq}$ for the reaction of **8**, combined with an extremely negative activation entropy $\Delta S^{\neq}$, indicates that in this case side reactions interfere with the splitting of $\Delta G^{\neq}$ into $\Delta H^{\neq}$ and $\Delta S^{\neq}$ terms.

In order to assess the reversibility of the primary H-transfer step (9) as a possible source of error, the reactions were also performed with D_2-labelled samples of **4**−**6** (RD_2) and [D_2]DHA, as described previously for DHA, **2**, and **3**. When the reactions were terminated after 50−75% turnover, no deuterium could be detected in the remaining **1**. This observation proves that the retrodisproportionation step (9) is irreversible under these conditions and that only this step is rate-determining.

The reaction mechanism outlined in Scheme 1 is supported by the large kinetic isotope effects that were measured with the deuterated samples of **4**−**6** (see Table 1). These are close to the maximum expected isotope effects for the retrodisproportionation step (9) at the temperatures

Table 1. Kinetics and thermochemistry of hydrogen transfer from polycyclic aromatic H-donors RH_2 **2**−**6** and **8** to α-methylstyrene **1** in diphenyl ether in the presence of an excess of 9,10-dihydroanthracene (DHA)[a]

H-Donor RH_2	k_{rel} [b] 240°C	$\Delta H_f°$(g) [c] (RH_2)	$\Delta H_f°$(g) [c] RH·	BDE [d] C−H	ΔH_R [e]	$\Delta H^{\neq}$ [f]	$\Delta S^{\neq}$ [f]	k_H/k_D [g] (°C)	$\Delta G^{\neq}$ kcal/mol
phenalene (**2**)[2]	3.87	51.4	70.0	70.6	26.3	21.5±0.1	−29.9±2.9	−	38.6±1.0
7*H*-benz[*de*]anthracene (**3**)[2]	≡1.00	64.3	88.5	76.2	31.9	23.8±0.9	−28.2±1.8	2.7 (250°C)	39.6±2.0
6*H*-benzo[*cd*]pyrene (**4**)	2.49	70.6	95.6	77.2	32.8	24.2±0.6	−25.7±1.2	2.3 (250°C)	38.9±0.9
7*H*-dibenz[*a*,*kl*]anthracene (**5**)	2.29	89.1	111.8	74.9	30.6	24.1±0.7	−26.0±1.3	1.8 (240°C)	39.0±1.0
4-methyl-7*H*-benz[*d*,*e*]naphthacene (**6**)	1.01	79.8	102.5	77.8	30.5	24.8±0.2	−26.3±0.5	2.1 (260°C)	39.8±0.4
4.5-methylenephenanthrene (**8**)[h]	0.003	76.5	113.9	89.8	45.1	(20.4±0.8)	(−44.4±1.2)	−	45.9±1.2
DHA[2]	0.01	38.2	69.1	80.0[i]	35.7	31.8±1.2	−21.5±2.1	2.1 (300°C)	44.1±1.2

[a] Energies in kcal·mol^{-1}; entropies in cal/K^{-1} mol^{-1}. − [b] Relative second-order rate constants for step (9) at 240°C. − [c] Heats of formation calculated with MOPAC 6.0 (AM1) RHF.[26] − [d] BDE (C−H) = $\Delta H_f°$ (RH·) − $\Delta H_f°$ (RH_2) + 52.10.[2,26b] − [e] Heat of reaction of the retrodisproportionation step (9).[2] − [f] Calculated from the second-order rate constants for step (9) over a temperature range of 40°C using the Eyring equation.[2] − [g] Primary kinetic isotope effect for step (9) by replacing RH_2 by RD_2 and DHA by [D_2]DHA at the temperatures indicated. − [h] In *sec*-butylbenzene without added DHA. − [i] Experimental value 83.0 kcal/mol,[27] see also ref.[26b]

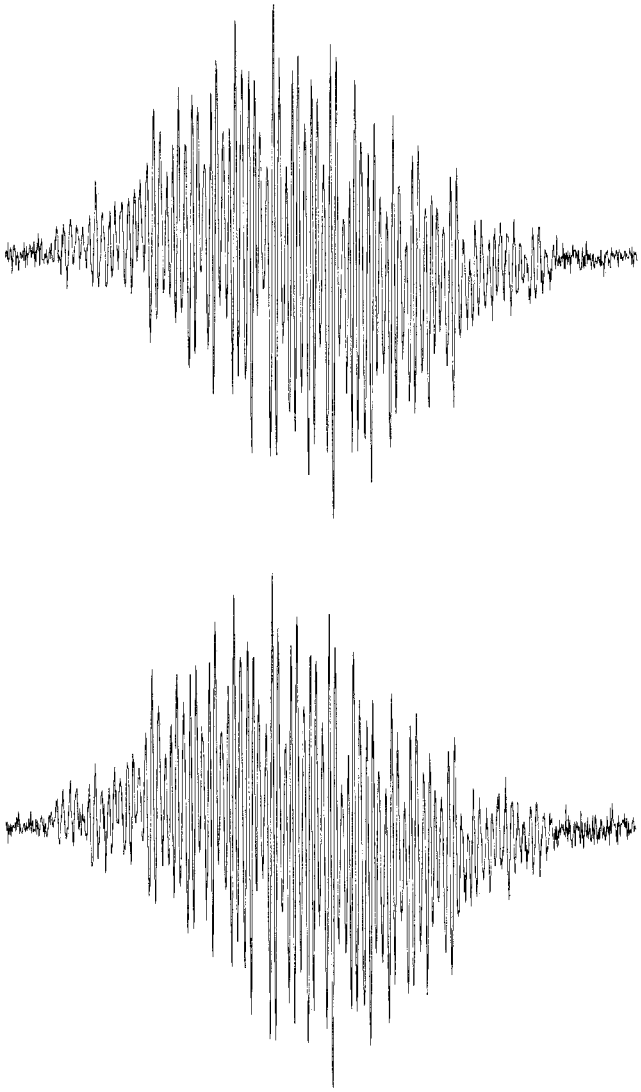


Figure 3. EPR spectra of 7*H*-dibenz[*a,kl*]anthracenyl radicals; (a) recorded during the transfer hydrogenation of **1** by **5** at 182°C; (b) monitored by heating **5** with di-*tert*-butyl peroxide at 160°C

recorded and support the assumption that H-transfer is approximately half complete in the transition state.[2]

By independent kinetic experiments using **4** and **1**, *p*-chloro-, *p*-methoxy-, and *p*-*tert*-butyl-α-methylstyrene at 250°C, it was found that the rates varied by less than a factor 1.5, which supports little charge separation in the transition state of (9). This befits an H-atom transfer rather than a hydride transfer mechanism. This is further supported by the negligible influence of solvent polarity on the rates of H-transfer to α-methylstyrene with **4** ($k_{\text{diphenyl ether}}$: $k_{\text{dimethylacetamide}}$: $k_{\text{benzonitrile}}$ = 1:0.9:0.9 at 250°C), **5** ($k_{\text{diphenyl ether}}$: $k_{\text{benzonitrile}}$ = 1:0.7 at 240°C), and **6** ($k_{\text{diphenyl ether}}$: $k_{\text{benzonitrile}}$ = 0.9 at 260°C).

In order to gain additional evidence for the formation of radical intermediates during the course of the reactions, EPR spectra were recorded. Due to the fast disproportionation of the 9-hydroanthryl radicals (Equation 12), their signals could not be detected. On the other hand, intense and well-resolved spectra of 6*H*-benzo[*cd*]pyrenyl and 7*H*-dibenzo[*a,kl*]anthracenyl radicals were obtained when transfer hydrogenations of **1** with **4** (at 177°C) or **5** (at 182°C) were performed in the cavity of the EPR spectrometer. At these temperatures, the radicals RH· (see Scheme 1) are in equilibrium with their dimers. Thus, their signals disappeared on cooling and reappeared on increasing the reaction temperature. The spectrum of the 6*H*-benzo[*cd*]pyrenyl radical was in excellent agreement with that published previously[23] and the coupling constants obtained by simulation were in good agreement with reported data.[24] The spectrum of the 7*H*-dibenzo[*a,kl*]anthracenyl radical was identified by its independent generation by heating **5** with di-*tert*-butyl peroxide at 160°C in degassed diphenyl ether in the cavity of the EPR spectrometer (Figure 3).

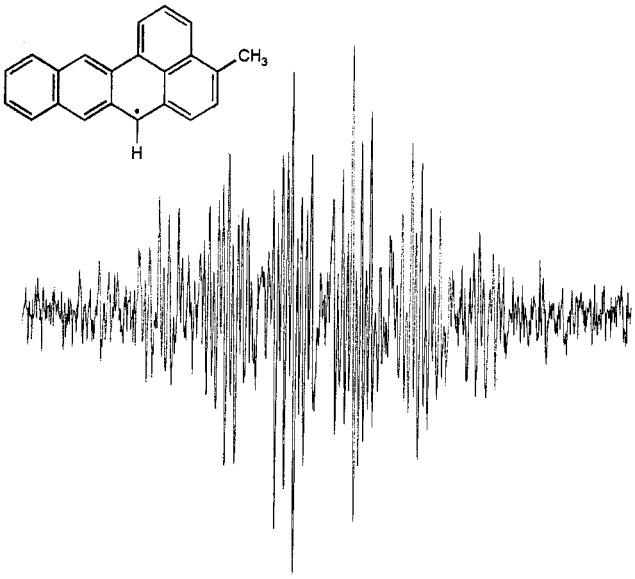


Figure 4. EPR spectrum of 4-methyl-7*H*-benzo[*de*]naphthacenyl radicals recorded during the transfer hydrogenation of **1** by **6** at 185°C

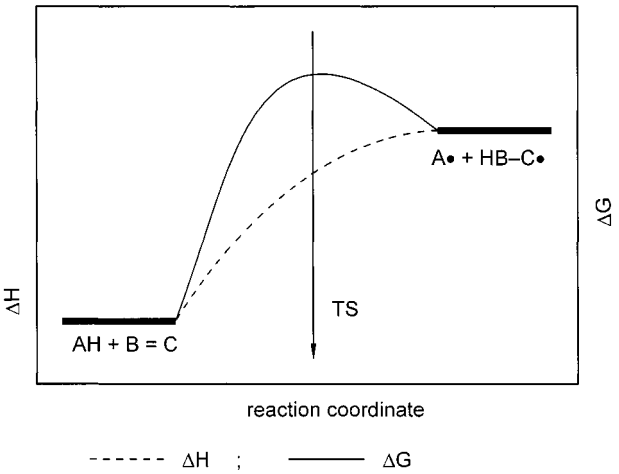


Figure 5. Schematic reaction coordinate of the transfer hydrogenation of **1** by H-donors **2**−**6**

When the transfer hydrogenation of **1** by **6** was performed at 185°C in the EPR spectrometer, a well-resolved spectrum

was also recorded, which was tentatively assigned to the 4-methyl-7*H*-benzo[*de*]naphthacenyl radical (see Figure 4). Attempts to generate this radical independently by heating **6** with di-*tert*-butyl peroxide were however unsuccessful, possibly due to the presence of the methyl group at C-4, which allows disproportionation.

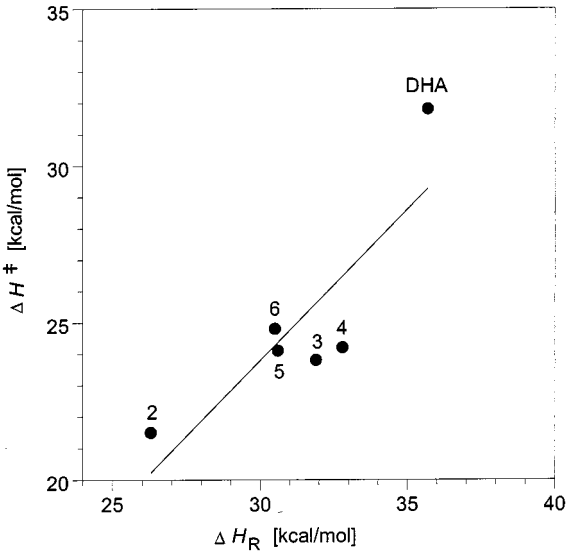


Figure 6. Correlation of the activation enthalpies $\Delta H^{\neq}$ for the transfer hydrogenation of **1** by **2**−**6** and DHA vs. the reaction enthalpies ΔH_R (AM1 results, see Table 1)

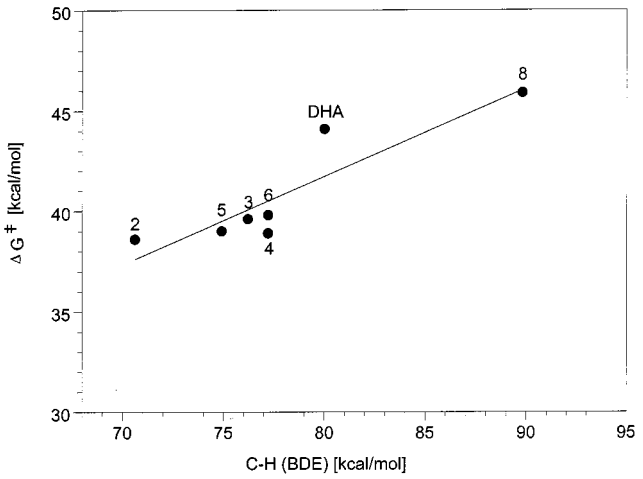


Figure 7. Correlation of the free activation enthalpies $\Delta G^{\neq}$ for the transfer hydrogenation of **1** by **2**−**6** and DHA vs. the bond energies BDE (C−H)

In similar experiments with **8**, no EPR spectra could be observed.

Discussion

The kinetic and EPR experiments reported herein strongly support the suggested mechanism based on Equations (9)−(12) for the "catalysis" of the transfer hydrogenation of **1** by the polycyclic hydrocarbons **2**−**6**. The key step of this transformation is the retrodisproportionation step (9), which determines the overall rate and the activation parameters. The latter are presented in Table 1. Because radical disproportionations, e.g. the reverse of step (1) or step (9) are diffusion-controlled processes,[25] they are assumed to proceed without an activation enthalpy $\Delta H^{\neq}$ [2] and, consequently, $\Delta H^{\neq}$ for retrodisproportionation must be equal to or lower than the reaction enthalpy $\Delta H_R{}^0$ (see Figure 5). Indeed, plots of $\Delta H^{\neq}$ vs. $\Delta H_R{}^0$ for the retrodisproportionation step (9) with H-donors **2**−**6** and DHA reveal an almost linear relationship between the two quantities (see Figure 6). The reaction enthalpies $\Delta H^0{}_R$ were derived in a consistent manner by AM1 calculations[26] (see Table 1). As found previously for a similar series of reactivities,[2] the slope of this correlation line is 0.9 and $\Delta H^{\neq}$ is invariably *smaller* than $\Delta H^0{}_R$.[2] As discussed in this previous paper,[2] the reactants do not have to surmount a ΔH barrier higher in energy than the products. The activation barrier $\Delta G^{\neq}$, however, is determined by the entropic term ($T\Delta S$), and hence the selectivity between dimerization and disproportionation is controlled by entropic factors, arising mainly from hindered internal rotations of the excited complexes.[25d] Consequently, the $\Delta G^{\neq}$ reaction coordinate in Figure 5 passes through an activation barrier due to $\Delta S^{\neq}$. Analysis of the kinetic data using the Eyring equation[2] is based on this $\Delta G^{\neq}$ transition state and thus reflects the dependence of the free enthalpy $\Delta G^{\neq}$ on the geometry (TS). Therefore, $\Delta H^{\neq}$ corresponding to this geometry is smaller than ΔH of the product radicals. This hypothesis is supported by the observation of large kinetic isotope effects, which can only be rationalized in terms of a transition state structure where the hydrogen atom is partially transferred.

The activation parameters for the reaction of **8** with **1** show a deviation from the plot depicted in Figure 6 and have therefore been disregarded. However, it is interesting to note that **8** does not show such a deviation when the relationship between $\Delta G^{\neq}$ and BDE (C−H) of the hydrogen donors is analyzed, as shown in Figure 7 (see Table 1). Although there is considerable scatter of the points in this plot, the general relationship outlined above in a qualitative way is irrefutable.

The $\Delta G^{\neq}$ values of these H-transfer reactions are seemingly more reliable than the $\Delta H^{\neq}$ and $\Delta S^{\neq}$ components derived from analysis of the Eyring equation. This has often been observed.

These results have important implications with regard to the coal liquefaction process,[11] which can be performed by heating finely ground coal with tetralin under hydrogen pressure. Besides thermal C−C cleavage reactions, transfer hydrogenations of the type discussed in this paper are also involved.[11b] Tetralin is a hydrogen donor, albeit of rather low reactivity. Structural elements of polycyclic aromatic hydrocarbons such as **2**−**7**, which have been reported to be present in coal, would seem likely to act as "catalysts" in the manner in which we have discussed. Indeed, their fixed position in the coal structure is probably even favorable since it may reduce the kinetic reaction order and the negative entropy effects on the rates. This hypothesis may help

to rationalize the comparatively low reaction temperatures of ca. 500°C required for coal liquefaction processes.

Experimental Section

General: ^{1}H NMR: Bruker WM 250 and WM 400 instruments. − FT IR: Perkin−Elmer Prodagon. − IR: Perkin−Elmer 398. − GC: Carlo−Erba GC 6000 apparatus, Vega Series 1 and 2 with FID; Carlo−Erba autosampler CTC-A 200; capillary columns: SE 30, 25 m (inner diameter: 0.32 mm, film thickness: 0.25 μm); N_2 flow: 2 mL/min; integrator: Hewlett−Packard 3390 A and 3392 A. − GC MS: Finnigan MAT 44s coupled to a Varian GC 3700 apparatus. − Thermolysis: Oil and tin thermostats (constructed in our laboratory); electronic temperature control unit: Lauda Ultrathermostat NB-315; temperature measurement: Pt 100/S 1220 from Systemtechnik AB. − EPR: Bruker BER-420 and EMX. − Melting points: Büchi Dr. Tottoli apparatus (uncorrected). − GC Conditions: Temperature program: 60°C (5 min.) − increment 10°C/min. − 250°C (20 min.).

EPR

General Procedures: (a) Observation of Radicals During Transfer Hydrogenations of 1: A solution of α-methylstyrene (**1**, 0.05−0.07 M), the appropriate hydrocarbon **4**−**6** (0.39−0.50 M), and 9,10-dihydroanthracene (DHA) in diphenyl ether was degassed by several "freeze-pump-thaw" cycles and then sealed under N_2 in an EPR sample tube (diameter: 2 mm, glass thickness: 1.0 mm). The tube was then placed in the cavity of an EPR spectrometer and heated to 160−185°C depending on the catalyst used. − **(b) Observation of Radicals by Heating 4−6 with Di-*tert*-butyl Peroxide:** A solution of the appropriate catalyst (0.2−0.5 M) and an equimolar amount of di-*tert*-butyl peroxide (filtered several times through neutral alumina prior to use) in diphenyl ether was thoroughly degassed and then sealed under N_2 in an EPR sample tube. Heating to the requisite temperature led to the observation of an EPR signal.

7*H*-Dibenzo[*a,kl*]anthracenyl Radical: (a) A mixture of α-methylstyrene (**1**, 0.09 m), 7*H*-dibenzo[*a,kl*]anthracene (**5**, 0.50 M), and DHA (1.02 M) in degassed diphenyl ether was submitted to the conditions outlined in general procedure (a), giving the spectrum depicted in Figure 3a. − Temperature: 182°C. − Center field: 3330.0 G. − Modulation frequency: 0.08 G. − Amplification: 1.12×10^6. − Frequency of the microwave: 9.346 GHz. − Microwave power: 6.331 mW. − Time constant: 82 ms. − Scan time: 671 s. − Sweep width: 50.0 G.

(b) A solution of **5** (0.07 M) and di-*tert*-butyl peroxide (0.07 M) in diphenyl ether was heated according to general procedure (b) (spectrum: see Figure 3b). − Temperature: 160°C. − Center field: 3330.0 G. − Modulation frequency: 0.07 G. − Amplification: 8.93×10^5. − Frequency of the microwave: 9.355 GHz. − Microwave power: 5.041 mW. − Time constant: 82 ms. − Scan time: 671 s. − Sweep width: 50.0 G.

4-Methyl-7*H*-benzo[*de*]naphthacenyl Radical: A mixture of the acceptor α-methylstyrene (**1**, 0.05 M), 4-methyl-7*H*-benzo[*de*]naphthacene (**6**, 0.39 M), and DHA (1.00 M) in diphenyl ether was submitted to the conditions of the general procedure (a) (spectrum: see Figure 4). − Temperature: 185°C. − Center field: 3331.4 G. − Modulation frequency: 0.05 G. − Amplification: 2.00×10^6. − Frequency of the microwave: 9.355 GHz. − Microwave power: 3.994 mW. − Time constant: 82 ms. − Scan time 1342 s. − Sweep width: 60.0 G.

X-ray Structural Analysis of 10:[29] Yellow crystals were grown from a solution in chlorobenzene: $C_{22}H_{14}O$, $M_r = 294.33$, $a = 8.1892(4)$, $b = 7.4693(2)$, $c = 24.0136(12)$ Å, $\beta = 93.368(2)°$, $V = 1466.32(11)$ Å^3, $Z = 4$, $d_{calcd} = 1.333$ Mg/m^3, crystal system: monoclinic, space group $P2_1/c$. Data collection and processing: crystal size: 1.1 × 0.22 × 0.06 mm, Enraf−Nonius Kappa-CCD diffractometer, $\lambda = 0.71074$ Å, collected reflections: 12434, independent: 3992 ($R_{int} = 0.044$), observed: 2262 [$I > 2\sigma(I)$], $\mu = 0.080$ mm^{-1}, no absorption correction. Solution by direct phase determination (SHELXS-97), full-matrix least-squares refinement on F^2 (SHELXL-97), hydrogen positions were refined isotropically; parameters 264, final indices [$I > 2\sigma(I)$]: $R = 0.0672$, $R_w^2 = 0.1737$, goodness-of-fit on F^2: 1.181, largest diff. peak: 0.191 eÅ^{-3}.

Computations: The enthalpies of formation were calculated with the MOPAC program (version 6.0)[26a] on an INDIGO R10000 computer. The AM1-RHF method was employed, using the keyword EF (eigenvector following) for optimization of the relevant structures. The input files were generated by molecular modelling using SYBYL.[30]

Materials: Diphenyl ether (99%), *sec*-butylbenzene (99%), benzonitrile (99%) and *N*-methylacetamide (99%) were purchased from Aldrich and thoroughly degassed with N_2. α-Methylstyrene (**1**; Aldrich, 99%), 4,5-methylenephenanthrene (**8**, Aldrich, 97%), benz[*a*]anthracene-7,12-dione (Aldrich, 97%), D_2O (Deutero GmbH, 99.9% D), $LiAlD_4$ (Aldrich, 98% D) and [D_1]ethanol (Aldrich, 99.5% D) were obtained commercially and used without further purification. 9,10-Dihydroanthracene (DHA, Janssen, 99%) was purified by repeated crystallization from water/acetone and anhydrous ethanol until no impurities could be detected by GC. − **Substituted α-Methylstyrenes: p**-Chloro-α-methylstyrene, *p*-methoxy-α-methylstyrene, and *p*-butyl-α-methylstyrene were prepared as described previously.[5] [D_4]DHA was obtained as described elsewhere.[2]

Synthesis of Hydrocarbons 4−8

6*H*-Benzo[*cd*]pyren-6-one:[21] A suspension of 20.0 g (98.9 mmol) of pyrene and 40.0 g (434.4 mmol) of glycerol in 320 g of 80% H_2SO_4 was heated in a water bath for 4 h. The black mixture was then poured into 500 mL of water and the resulting suspension was filtered through paper over a period of 3 days, leading to a dark-green residue. The crude product was refluxed in 1.6 L of 1% NaOH, affording a yellow suspension. Collection of the product by filtration, followed by chromatography on silica gel (1.2 m × 10 cm) with $CHCl_3$ as eluent gave 6*H*-benzo[*cd*]pyren-6-one as yellow leaflets. Yield: 8.2 g (32.2 mmol, 33%; ref.[21] 40%); m.p. 243−244°C (ref.[21] 243°C); purity > 99% (GC). − IR (KBr): $\tilde{\nu}$ = 3050 cm^{-1} (aryl-H), 1648 (C=O), 1606, 1568 (C=C); 1282, 835, 750 (aryl-H). − ^{1}H NMR (250 MHz, $CDCl_3$/TMS): δ = 7.86 (t, $J = 7.7$ Hz, 2 H, 4-,7-H), 7.95 (d, $J = 8.7$ Hz, 2 H, 1-,10-H), 8.06 (d, $J = 8.7$ Hz, 2 H, 2-,9-H), 8.28 (dd, $J = 7.3$ Hz, $J = 1.2$ Hz, 2 H, 3-,8-H), 8.84 (dd, $J = 7.3$ Hz, $J = 1.2$ Hz, 2 H, 5-,6-H). − MS (EI, 70 eV): *m/z* (%) = 254 (100) [M^+].

6*H*-Benzo[*cd*]pyrene (4):[17] At 0°C, 0.72 g (18.5 mmol) of $LiAlH_4$ and 5.07 g (673.9 mmol) of $AlCl_3$ were added portionwise to 40 mL of dry diethyl ether. A solution of 1.38 g (5.43 mmol) of 6*H*-benzo[*cd*]pyren-6-one in 40 mL of absolute benzene was then slowly added to the stirred suspension. The addition of each drop produced a transient red color, which vanished immediately upon stirring. The reaction mixture was stirred for a further 2 h and then poured into 20 mL of ice-cold dilute aq. H_2SO_4. The phases were separated and the organic layer was washed with water (3 × 50 mL). Drying of the ethereal phase with Na_2SO_4 and evaporation of the solvent afforded a yellow residue, which was crystallized from

cyclohexane to yield yellow needles. On the basis of its symmetrical ^{1}H-NMR spectrum, the product was not an isomeric mixture,[16] but rather pure compound **4**. Yield: 1.20 g (4.99 mmol, 92%; ref.[16] 97%); m.p. 123−124°C (ref.[16] 120−130°C); purity (GC): > 99%. − IR (KBr): $\tilde{\nu}$ = 3048 cm^{-1} (aryl-H), 1592 (C=C), 1130, 835, 762 (aryl-H). − ^{1}H NMR (400 MHz, $CDCl_3$/TMS): δ = 4.98 (s, 2 H, CH_2), 7.40−7.47 (m, 2 H, 5-,6-H), 7.48−7.52 (m, 2 H, 4-,7-H), 7.73 (dd, *J* = 7.7 Hz, *J* = 1.1 Hz, 2 H, 3-,8-H), 7.76 (d, *J* = 8.6 Hz, 2 H, 2-,9-H), 7.80 (d, *J* = 8.6 Hz, 2 H, 1-,10-H). − ^{13}C NMR (100 MHz, $CDCl_3$/TMS): δ = 34.31 (CH_2), 125.36, 125.61, 126.04, 126.44, 126.75, 126.95, 127.99, 128.12, 132.05, 134.04. − $C_{19}H_{12}$: calcd. C 94.97, H 5.03; found C 94.15, H 5.09.

7*H*-Dibenz[*a,kl*]anthracen-7-one (9b):[17] 20.0 g (77 mmol) of benz[*a*]anthracene-7,12-dione and 20.3 g (218 mmol) of aniline were suspended in 460 g of 80% H_2SO_4. The mixture was maintained at 50°C while 56.1 g (609 mmol) of glycerol was added dropwise. The reaction mixture was then kept at 100°C for 12 h, cooled to 25°C, hydrolyzed with 1 L of water, and filtered through paper. The collected brown residue was washed with hot water and dried under reduced pressure. The crude product was extracted with 300 mL of hot acetone, and removal of the solvent from the extract afforded 5.9 g of a mixture of three isomers. Attempts to separate the isomers by chromatography on silica gel using various eluent systems were unsuccessful. Pure **9b** was finally obtained by repeated crystallization from a large excess of dry pyridine. Yield: 3.4 g (12.1 mmol, 16%; ref.[17] 13%); m.p. 188°C (ref.[17] 188−189°C); purity (GC): 99%. − IR (KBr): $\tilde{\nu}$ = 3050 cm^{-1}, 3022 (aryl-H), 1648 (C=O), 1612, 1596, 1572 (C=C), 1268, 813, 792, 762, 741 (aryl-H). − ^{1}H NMR (250 MHz, $CDCl_3$/TMS): δ = 7.46−7.53 (m, 1 H, aryl-H), 7.53−7.61 (m, 1 H, aryl-H), 7.61−7.74 (m, 2 H, aryl-H), 7.78 (dd, *J* = 7.9 Hz, *J* = 1.5 Hz, 1 H, aryl-H), 7.90 (d, *J* = 7.9 Hz, 1 H, aryl-H), 8.01 (d, *J* = 8.9 Hz, 1 H, aryl-H), 8.08 (dd, *J* = 8.2 Hz, *J* = 1.2 Hz, 1 H, aryl-H), 8.28 (d, *J* = 9.2 Hz, 1 H, aryl-H), 8.40 (d, *J* = 7.3 Hz, 1 H, aryl-H), 8.68 (dd, *J* = 7.5 Hz, *J* = 1.4 Hz, 1 H, aryl-H), 9.93 (dd, *J* = 8.9 Hz, *J* = 0.9 Hz, 1 H, aryl-H). − ^{13}C NMR (100 MHz, $CDCl_3$/TMS): δ = 121.48, 124.53, 126.07, 126.39, 126.79, 127.04, 127.07, 127.15, 127.20, 128.51, 129.06, 129.51, 129.75, 131.08, 131.33, 132.07, 133.08, 134.80, 134.91, 137.43, 185.15. − MS (EI, 70 eV): *m/z* (%) = 280 (100) [M$^+$]. − $C_{21}H_{12}O$: calcd. C 89.98, H 4.32; found C 89.74, H 4.35.

7*H*-Dibenz[*a,kl*]anthracene (5): To 80 mL of dry diethyl ether at 0°C were added 1.01 g (22.5 mmol) of $LiAlH_4$, 6.12 g (45.9 mmol) of $AlCl_3$, and 1.20 g (4.3 mmol) of 7*H*-dibenz[*a,kl*]anthracen-7-one (**9b**). The resulting suspension was stirred at room temperature under N_2 for 12 h. It was then poured into a mixture of 50 g of crushed ice and 20 mL of 2 N HCl. The organic layer was separated and the aqueous layer was extracted with diethyl ether (3 × 30 mL). The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated in vacuo, to afford bright-yellow crystals. Yield: 1.08 g (4.05 mmol, 95%); m.p. 167−168°C (ref.[19] 89.5−90.5°C); purity (GC): 99%. − IR (KBr): $\tilde{\nu}$ = 3052 cm^{-1} (aryl-H), 2920 (alkyl-H), 1593, 1560 (C=C), 800, 770, 741, 668 (aryl-H). − ^{1}H NMR (400 MHz, $CDCl_3$/TMS): δ = 4.98 (s, 2 H, CH_2), 7.44−7.52 (m, 4 H, aryl-H), 7.55−7.60 (m, 1 H, aryl-H), 6.67 (dd, *J* = 7.9 Hz, *J* = 1.3 Hz, 1 H, aryl-H), 7.70 (d, *J* = 7.9 Hz, 1 H, aryl-H), 7.80 (d, *J* = 8.8 Hz, 1 H, aryl-H), 7.83−7.86 (m, 1 H, aryl-H), 8.03 (d, *J* = 7.5 Hz, 1 H, aryl-H), 8.09−8.13 (m, 1 H, aryl-H), 8.16 (d, *J* = 8.8 Hz, 1 H, aryl-H). − ^{13}C NMR (100 MHz, $CDCl_3$/TMS): δ = 31.47 (CH_2), 119.34, 120.27, 121.51, 122.50, 123.50, 125.18, 125.23, 125.61, 125.98, 126.21, 126.45, 126.66, 127.44, 127.67, 128.59, 128.89, 132.01, 133.09, 133.27, 134.07.

4-Methylbenzo[*de*]naphthacen-7-one (10):[20] To a mixture of 9.2 g (64.7 mmol) of 1-methylnaphthalene and 15.3 g (114.8 mmol) of $AlCl_3$ in absolute carbon disulfide, 10.1 g (53.0 mmol) of 2-naphthoyl chloride was added in small portions. The black mixture was stirred at room temperature for 12 h and then hydrolyzed with 50 g of ice and 20 mL of 2 N HCl. The resulting mixture was stirred for a further 2 h, until the complex was fully decomposed. It was then filtered and the filtrate was concentrated under reduced pressure to afford a brownish residue, which was crystallized from acetic acid and chlorobenzene. The product was obtained as orange-colored needles. Yield: 9.20 g (31.2 mmol, 59%; ref.[20] 69%); m.p. 203−205°C (ref.[20] 207°C); purity (GC): 97%. − IR (KBr): $\tilde{\nu}$ = 3042 cm^{-1} (aryl-H), 2915 (alkyl-H), 1658 (C=O), 1620, 1585, 1575 (C=C), 880, 848, 772, 735 (aryl-H). − ^{1}H NMR (250 MHz, $CDCl_3$/TMS): δ = 2.80 (s, 3 H, CH_3), 7.48−7.63 (m, 3 H, aryl-H), 7.64−7.72 (m, 1 H, aryl-H), 7.94 (d, *J* = 8.2 Hz, 1 H, aryl-H), 8.03 (d, *J* = 7.9 Hz, 1 H, aryl-H), 8.09 (d, *J* = 8.2 Hz, 1 H, aryl-H), 8.53 (d, *J* = 7.3 Hz, 1 H, aryl-H), 8.63 (d, *J* = 7.3 Hz, 1 H, aryl-H), 8.67 (s, 1 H, aryl-H), 8.98 (s, 1 H, aryl-H). − ^{13}C NMR (100 MHz, $CDCl_3$/TMS): δ = 20.33 (CH_3), 122.23, 122.93, 125.46, 126.06, 126.63, 127.08, 127.29, 127.44, 128.22, 128.40, 128.70, 128.96, 129.22, 129.68, 132.03, 132.07, 132.21, 135.51, 142.66, 183.71. − $C_{22}H_{14}O$: calcd. C 89.77, H 4.79; found C 89.57, H 4.67.

4-Methyl-7*H*-benzo[*de*]naphthacene (6): At 0°C, 540 mg (12.0 mmol) of $LiAlH_4$ and 6.12 g (45.9 mmol) of $AlCl_3$ were added to 60 mL of dry diethyl ether. To the stirred suspension, 1.02 g (3.5 mmol) of 4-methylbenzo[*de*]naphthacen-7-one (**10**) was added in small portions. Stirring was continued at room temperature for 16 h. The reaction mixture was then poured into ice (50 g) and 2 N HCl (10 mL) and extracted with dichloromethane (3 × 30 mL). The combined organic layers were washed thoroughly with water, dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was recrystallized from dry chlorobenzene to afford **6** as yellow needles. Yield: 823 mg (2.9 mmol, 83%); m.p. 159−161°C; purity (GC): 99%. − IR (KBr): $\tilde{\nu}$ = 3052 cm^{-1}, 3030, 3012 (aryl-H), 2960, 2940, 2850 (alkyl-H), 1560, 1497 (C=C), 954, 833, 812, 747 (aryl-H). − ^{1}H NMR (400 MHz, $CDCl_3$/TMS): δ = 2.67 (s, 3 H, CH_3), 4.64 (s, 2 H, CH_2), 7.29−7.31 (m, 2 H, aryl-H), 7.39−7.43 (m, 2 H, aryl-H), 7.57−7.62 (m, 1 H, aryl-H), 7.73−7.77 (m, 2 H, aryl-H), 7.85−7.89 (m, 1 H, aryl-H), 7.93 (dd, *J* = 8.3 Hz, *J* = 1.1 Hz, 1 H, aryl-H), 8.28 (d, *J* = 7.2 Hz, 1 H, aryl-H), 8.49 (s, 1 H, aryl-H). − ^{13}C NMR (100 MHz, $CDCl_3$/TMS): δ = 19.66 (CH_3), 34.65 (CH_2), 119.39, 122.61, 124.19, 124.34, 125.60, 126.12, 126.23, 126.70, 126.80, 126.96, 128.34, 131.09, 131.50, 131.86, 132.90, 133.21. − MS (EI, 70 eV): *m/z* (%) = 280 (52) [M$^+$].

3-Benzoylpyrene:[21] At room temperature, 20.04 g (150 mmol) of $AlCl_3$ was added portionwise to a well-stirred solution of 20.05 g (99 mmol) of pyrene and 15.08 g (107 mmol) of benzoyl chloride in absolute benzene. The color changed from yellow to red, while the temperature increased to 35°C. After stirring for a further 2 h, the mixture was cooled to 0°C and 250 mL of water was added. The phases were separated, the organic layer was concentrated under reduced pressure, and the oily residue was dried in vacuo. Boiling in 1 L of dry ethanol, hot filtration, and removal of the solvent afforded the crude product, which was recrystallized twice from absolute ethanol. Yield: 16.45 g (54 mmol, 54%); m.p. 124−126°C (ref.[21] 128°C); purity (GC): 99%. − IR (KBr): $\tilde{\nu}$ = 3044 cm^{-1} (aryl-H), 1648 (C=O), 1594, 1506 (C=C), 830, 726, 706, 682 (aryl-H). − ^{1}H NMR (250 MHz, $CDCl_3$/TMS): δ = 7.41−7.50 (m, 2 H, aryl-H), 7.56−7.64 (m, 1 H, aryl-H), 7.85−7.92 (m, 2 H, aryl-H), 7.99−8.25 (m, 8 H, aryl-H), 8.34 (d, *J* = 9.5 Hz, 1 H, aryl-H).

Dibenzo[*b,fg*]pyren-8-one:[21] Under stirring, 10.1 g (33 mmol) of 3-benzoylpyrene was added portionwise to a melt of 83.2 g (624 mmol) of $AlCl_3$ and 12.7 g (294 mmol) of NaCl at 120°C. On

Table 2. Kinetics of the transfer hydrogenation of substituted α-methylstyrenes (*p*-X)-**1** by the hydrocarbons RH_2 (**4**−**6** and **8**) in the presence of DHA in various solvents

T[a] [°C]	RH_2 [M]	**1** [M]	DHA [M]	Solvent[b]	$10^4 k_2$ [c] [$S^{-1}M^{-1}$]	± σ %	mass balance %
RH_2 = 6*H*-benzo[*cd*]pyrene **4**							
219.9	0.21	0.08	1.00	DE	4.687	1.0	99
230.1	0.21	0.08	1.00	DE	7.655	0.9	97
240.1	0.21	0.08	1.00	DE	13.101	0.8	99
250.0	0.21	0.08	1.00	DE	20.713	1.2	99
260.0	0.21	0.08	1.00	DE	30.690	2.0	99
250.0	0.15	0.07	1.00	DE	18.364	1.0	97
249.9	0.30	0.08	1.00	DE	19.520	1.1	100
250.1	0.40	0.08	1.00	DE	19.443	2.1	98
250.0[d]	0.21	0.08	1.00	DE	8.823	1.6	99
250.0[e]	0.21	0.08	1.00	DE	31.835	1.2	98
249.9[f]	0.21	0.08	1.00	DE	21.251	1.8	99
250.2[g]	0.21	0.08	1.00	DE	27.353	2.3	99
249.9	0.21	0.08	1.00	*N*-Me	17.685	3.3	99
250.0	0.21	0.08	1.00	BN	18.656	2.2	98
RH_2 = 7*H*-dibenz[*a*,*kl*]anthracene **5**							
200.0	0.50	0.09	1.02	DE	1.475	2.4	99
210.0	0.50	0.09	1.02	DE	2.431	1.8	99
220.1	0.50	0.09	1.02	DE	4.373	2.1	99
230.1	0.50	0.09	1.02	DE	6.738	2.1	99
240.4	0.50	0.09	1.02	DE	12.090	2.1	99
240.1	0.50	0.09	1.00	BN	9.058	1.3	98
239.9[h]	0.45	0.08	1.00	DE	6.742	1.7	99
RH_2 = 4-methyl-7*H*-benz[*de*]naphthacene **6**							
219.7	0.39	0.05	1.00	DE	1.879	1.4	98
229.7	0.39	0.05	1.00	DE	3.101	1.6	98
239.8	0.39	0.05	1.00	DE	5.340	1.8	98
250.1	0.39	0.05	1.00	DE	8.610	2.5	98
260.2	0.39	0.05	1.00	DE	13.834	2.2	100
260.2	0.38	0.07	1.00	BN	12.055	2.0	99
260.3[i]	0.39	0.08	1.00	DE	6.754	2.0	99
RH_2 = 4,5-methylenephenanthrene **8**							
329.7	1.01	0.07	−	*sec*. B	0.959	2.8	85
330.1	1.01	0.07	−	*sec*. B	1.244	3.6	85
350.0	1.01	0.07	−	*sec*. B	1.674	3.7	94
361.4	1.01	0.07	−	*sec*. B	2.237	3.8	94
370.5	1.01	0.07	−	*sec*. B	3.059	2.7	98
360.7	0.49	0.05	−	*sec*. B	2.689	3.8	70
361.7	2.01	0.08	−	*sec*. B	3.008	3.2	83

[a] Reaction temperature ±0.2°C. − [b] DE = diphenyl ether; BN = benzonitrile; N-Me = *N*-methylacetamide; *sec*. B = *sec*-butylbenzene. − [c] Second-order rate constants for step (9) corrected for volume expansion during heating. − [d] $[D_2]$-**4** and $[D_4]$DHA. − [e] p-Cl-**1**. − [f] p-*tert*-butyl-**1**. − [g] p-CH_3O-**1**. − [h] $[D_2]$-**5** and $[D_4]$DHA. − [i] $[D_2]$-**6** and $[D_4]$DHA.

heating to 170°C for 15 min., the color changed from black to dark-red. The reaction mixture was then allowed to cool to room temperature and 100 mL water was added in small portions under vigorous stirring, giving an aggregated precipitate. Boiling in 2 N HCl and subsequent filtration afforded a brown solid, which was boiled in 100 mL of water, filtered once more, and dried under reduced pressure. The crude product was then dissolved in 80 mL of hot absolute nitrobenzene, yielding brown crystals on cooling. After storage of the mother liquor at 4°C for 16 h, a second crop of the product was obtained. Filtration through neutral alumina with CH_2Cl_2 as eluent and evaporation of the solvent afforded the product, which was recrystallized twice from dry chlorobenzene to yield orange-colored needles. Yield: 2.58 g (8.9 mmol, 27%); m.p. 245−248°C (ref.[21] 242°C); purity (GC): 99%. − IR (KBr): $\tilde{\nu}$ = 3045 cm^{-1} (aryl-H), 1697 (C=O), 1610, 1599 (C=C), 845, 798, 758, 697 (aryl-H). − ^{1}H NMR (250 MHz, $CDCl_3$/TMS): δ = 7.27−7.35 (m, 1 H, aryl-H), 7.45−7.53 (m, 1 H, aryl-H), 7.67−7.72 (m, 2 H, aryl-H), 7.95 (t, *J* = 7.6 Hz, 1 H, aryl-H), 8.02 (d, *J* = 9.1 Hz, 1 H, aryl-H), 8.10−8.26 (m, 5 H, aryl-H), 9.21 (d, *J* = 9.1 Hz, 1 H, aryl-H). − MS (EI, 70 eV): *m/z* (%) = 304 (46) [M^+]. − $C_{23}H_{12}O$: calcd. C 90.77, H 3.97; found C 90.71, H 3.94.

8*H*-Dibenzo[*b*,*fg*]pyrene (7): At 0°C, 200 mg (4.5 mmol) of $LiAlH_4$ and 2.10 g (15.8 mmol) of $AlCl_3$ were added to 50 mL of dry diethyl ether. To the stirred suspension was added 500 mg (1.6 mmol) of dibenzo[*b*,*fg*]pyren-8-one and the mixture was stirred under nitrogen at 25°C for 18 h. After quenching with ice and 2 N HCl, the organic phase was separated and the aqueous layer was extracted with dichloromethane (3 × 30 mL). The combined organic phases were dried over Na_2SO_4, filtered, and the filtrate was concentrated under reduced pressure. Chromatography of the crude product on silica gel (elution with cyclohexane/dichloromethane, 2:1) afforded yellow needles. Yield: 390 mg (1.3 mmol, 81%); m.p. 219−220°C; purity (GC): >99%. − IR (KBr): $\tilde{\nu}$ = 3020 cm^{-1} (aryl-H), 1428, 839, 820, 702 (aryl-H). − ^{1}H NMR (250 MHz, $CDCl_3$/TMS): δ = 4.41 (s, 2 H, $>CH_2$), 7.41 (td, *J* = 7.3 Hz, *J* = 1.2 Hz, 1 H, aryl-H), 7.44−7.53 (m, 1 H, aryl-H), 7.71 (d, *J* = 6.7 Hz, 1 H, aryl-H), 7.93−8.24 (m, 8 H, aryl-H), 8.54 (s, 1 H, 13-H). − ^{13}C NMR

(100 MHz, $CDCl_3$/TMS): δ = 35.61 (>CH_2), 116.14, 120.37, 123.75, 124.02, 125.14, 125.16, 125.22, 125.53, 127.00, 127.13, 127.34, 127.86, 127.93, 130.91, 131.04, 131.21, 137.83, 139.59, 142.36, 143.65. − MS (EI, 70 eV): *m/z* (%) = 290 (46) [M^+].

Synthesis of Deuterated 4−6. − General Procedure: At 0°C, $LiAlD_4$ (2 mmol) and $AlCl_3$ (4 mmol) were suspended in 15 mL of anhydrous diethyl ether. The ketone (0.5 mmol) was gradually added and the mixture was stirred under nitrogen for 12 h. Under exclusion of air and moisture, 5 mL of D_2O was added and stirring was continued for a further 30 min. After separation of the phases, the aqueous layer was extracted with diethyl ether (3 × 30 mL). The combined organic phases were dried over Na_2SO_4, filtered, and the solvent was removed under reduced pressure to leave a yellow solid. The crude product was purified by passage through a column of silica gel with cyclohexene/dichloromethane (2:1) as eluent. Evaporation of the solvent afforded the crystalline product, which was dried in vacuo.

[D_2]-6*H*-Benzo[*cd*]pyrene ([D_2]-4): 135 mg (0.5 mmol) of 6*H*-benzo[*cd*]pyren-6-one (**10**) was submitted to the conditions of the general procedure using 80 mg (2.0 mmol) of $LiAlD_4$ and 510 mg (3.8 mmol) of $AlCl_3$ in 20 mL of dry diethyl ether. Yield: 96.8 mg (0.40 mmol, 76%); m.p. 115−116°C; purity (GC): 96%; deuteration of the methylene protons 99% (NMR). − ^{1}H NMR (250 MHz, $CDCl_3$/TMS): δ = 4.98 (m, <0.02 H, CH_2), 7.40−7.47 (m, 2 H, 5-,6-H), 7.50 (t, *J* = 7.7 Hz, 2 H, 4-,7-H), 7.73 (dd, *J* = 7.7 Hz, *J* = 1.1 Hz, 2 H, 3-,8-H), 7.76 (d, *J* = 8.6 Hz, 2 H, 3-,8-H), 7.80 (d, *J* = 8.6 Hz, 2 H, 5-,6-H).

[D_2]-7*H*-Dibenz[*a,kl*]anthracene ([D_2]-5): 130 mg (0.46 mmol) of 7*H*-dibenz[*a*,*kl*]anthracen-7-one (**9b**) was transformed according to the general procedure using 70 mg (1.4 mmol) of $LiAlD_4$ and 501 mg (3.8 mmol) of $AlCl_3$ in 15 mL of dry diethyl ether. Yield: 108 mg (0.40 mmol, 87%); m.p. 162−163°C; purity (GC): 99%; deuteration of the methylene protons > 97% (NMR). − IR (KBr): $\tilde{\nu}$ = 3052 cm^{-1}, 3028 (aryl-H), 2925, 2854 (alkyl-H), 1592 (C=C), 840, 775, 749 (aryl-H). − ^{1}H NMR (250 MHz, [D_6]DMSO): δ = 4.52 (m, <0.06 H, CH_2), 7.27−7.56 (m, 6 H, aryl-H), 7.72 (dd, *J* = 8.5 Hz, *J* = 1.8 Hz, 1 H, aryl-H), 7.75−7.81 (m, 1 H, aryl-H), 8.08−8.16 (m, 2 H, aryl-H).

[D_2]-4-Methylbenzo[*de*]naphthacene ([D_2]-6): Reduction of 400 mg (1.6 mmol) of 4-methylbenzo[*de*]naphthacen-7-one (**10**) was carried out according to the general procedure using 260 mg (5.3 mmol) of $LiAlD_4$ and 1.53 g (11.8 mmol) of $AlCl_3$ in 24 mL of anhydrous diethyl ether. Yield: 334 mg (1.2 mmol, 75%); m.p. 155−156°C; purity (GC): 99%; deuteration of the methylene protons > 95% (NMR). − IR (KBr): $\tilde{\nu}$ = 3052 cm^{-1} (aryl-H), 2910, 2850 (alkyl-H), 1596 (C=C), 882, 789, 754, 742 (aryl-H). − ^{1}H NMR (250 MHz, $CDCl_3$/TMS): δ = 2.67 (s, 3 H, CH_3), 4.64 (s, <0.1 H, CH_2), 7.28−7.33 (m, 2 H, aryl-H), 7.40−7.45 (m, 2 H, aryl-H), 7.57−7.65 (m, 1 H, aryl-H), 7.73−7.78 (m, 2 H, aryl-H), 7.85−7.91 (m, 1 H, aryl-H), 7,95 (d, *J* = 8.3 Hz, 1 H, aryl-H), 8.29 (d, *J* = 7.3 Hz, 1 H, aryl-H), 8.50 (s, 1 H, aryl-H). − MS (EI, 70 eV): *m/z* (%) = 282 (32) [M^+].

Kinetics: Kinetic measurements were made according to procedures reported in detail in previous papers.[9][10] The data in Table 1 are based on the results of kinetic runs presented in Table 2.

The Eyring parameters included in Table 1 were calculated by weighted linear least-squares calculations. The weighting factors were calculated on a log scale from the standard deviations of the *k* values.[31]

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