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Bimolecular Formation of Radicals by Hydrogen Transfer. 14 [1]

The Uncatalyzed Transfer Hydrogenation of α-Methylstyrene by 2,6-disubstituted 9,10-Dihydroanthracenes

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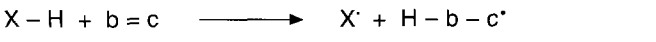
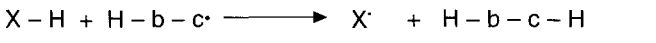
Abstract. 2,6-Dimethoxy- (**4a**), 2,6-bis(dimethylamino)- (**4b**), 2,6-dichloro- (**4c**) and 2,6-dimethoxycarbonyl-9,10-dihydroanthracene (**4d**) were prepared by conventional methods and used as hydrogen transfer donors to α-methylstyrene (**5**) between 290 – 350 °C. The mechanism followed second order kinetics and the rate constants were only slightly influenced by the solvent polarity and the type of substituents introduced. The activation parameters are also closely similar in the series with $\Delta S^{\neq}$ values between −21 and −28 cal/mol K. These results, together with the observation of a large isotope effect (k_H/k_D = 1.4 – 2.0 at 310 – 350 °C), suggest that the mechanism involves a primary kinetic H-atom-transfer from the donors to α-methylstyrene (**5**) in the rate determining step. The compounds **4a** – **4d** constitute a new probe for investigating polar effects on H-transfer reactions.

It has been shown in a recent review [2] that many hydrogen transfer reactions – some of them new, others well established ones – follow an unexpected common mechanistic pattern: They are initiated by an H-atom transfer from a donor with a weak X-H bond to an unsaturated acceptor b=c.



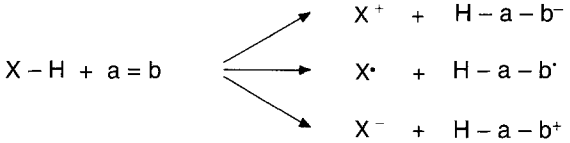
This step is the reverse of a radical disproportionation and, therefore, called "retrodisproportionation". It is generally followed by a normal radical H-transfer reaction *e.g.*



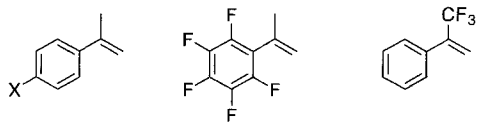
and the radicals X· are consumed by dimerisation or disproportionation. The overall reaction, generally, is a stepwise non-chain process but radical chains, electron transfer or other side reactions may interfere. Suitable donors are *e.g.* 9,10-dihydroanthracene, xanthene, acridane, phenalene, [7*H*]benz[*de*]anthracene and others. Suitable acceptors are alkenes of the styrene type, conjugated dienes, azo- and azoxy-, nitro- and nitroso-compounds or quinones [2].

In the mechanistic study of these reactions the clear distinction between H-atom transfer or electron or hydride transfer was the main issue [2]. The development of convincing mechanistic criteria for this distinction is important, because it also is relevant for biochemical hydrogenation and dehydrogenation reactions *e.g.* by NADH or NADPH. The long-standing controversy of electron transfer *vs.* hydride transfer has been recently augmented by the postulation of a proton coupled electron transfer, which seems hardly distinguishable from H-atom transfer [2, 3]. It is interesting to note that the structures of the transition states of these and also of similar proton transfer processes as obtained from MO-calculations are very similar and dispose a small positive charge on the hydrogen atom [2, 4].

A typical mechanistic probe for charge separation is the influence of substituents on reaction rates.



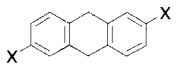
Previously, we found that the rates of transfer hydrogenations of α-methylstyrene are little changed when substituents are introduced into the aromatic ring or the methyl group of α-methylstyrene revealing no charge development in the styrene unit [5].



X = *t*-Bu, CH_3O, Cl, CN

The H-donor was tested for charge development by comparing the rates of the hydrogen donation from DHA to α-methylstyrene (**5**) with that of xanthene or acridane. The observed small rate effects correlate reasonably well with homolytic C–H bond energies of the donors and in no way with the heterolytic bond energies. Even when polar quinones were used as hydrogen acceptors only minor polar effects were observed [6].

In order to have an additional tool for investigating substituent effects of a series of H-donors we prepared the 2,6-disubstituted 9,10-dihydroanthracenes **4a–4d**. This series has the advantage over the use of xanthene and acridane that the second and third step of the transfer hydrogenations of α-methylstyrene (**5**) are precisely the same as those proposed for 9,10-dihydroanthracene DHA (Scheme 1). For a hydride or proton transfer σ^+ or σ^- correlations of the rates with large ρ values must be expected but not for H-atom transfer [7].



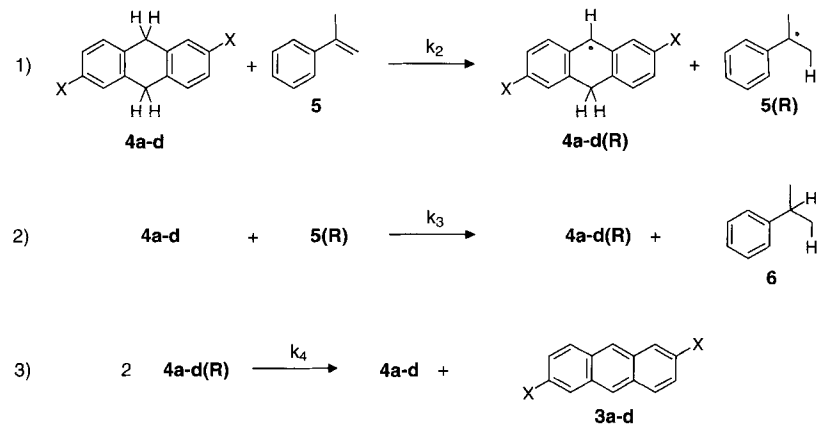
	X
4a	OCH_3
4b	$N(CH_3)_2$
4c	Cl
4d	$COOCH_3$

Synthesis

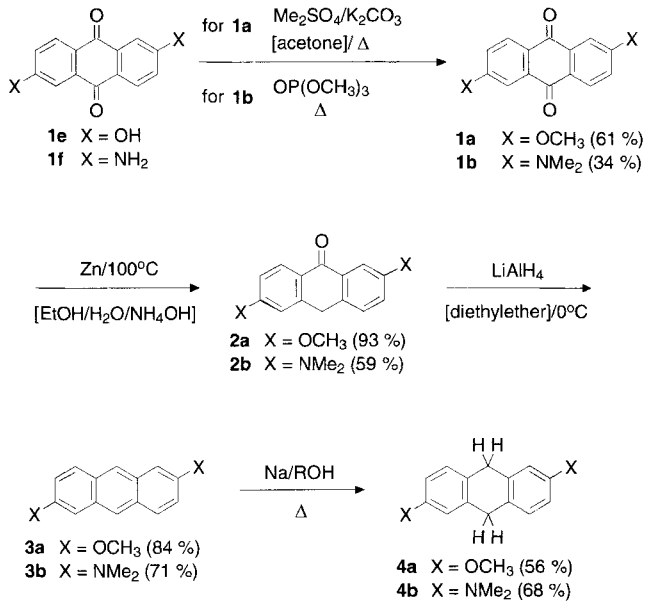
The procedures previously used for the synthesis of 2,6-dimethoxy-9,10-dihydroanthracene (**4a**) [8] could not be reproduced in good yields. **3a** was prepared, therefore, by the procedures given in Scheme 2. It was hydrogenated with sodium in ethanol to 2,6-dimethoxy-9,10-dihydroanthracene (**4a**) in 56% yield. The NMR-spectrum did not show the dynamic phenomena of the protons at C-9 and C-10 which were reported earlier for a sample prepared by another route [8]. Because the melting point reported in ref. [8] deviates by 100 °C from our's we attempted to repeat the one step synthesis of **4a** by a condensation reaction of *p*-methoxybenzyl alcohol as reported. However, **4a** could not be successfully isolated from the complex product mixture which contained only 4% of **4a** according to gc.

2,6-Bis(dimethylamino)-9,10-dihydroanthracene (**4b**) was synthesized in a similar way in four steps as shown in Scheme 2.

To the best of our knowledge 2,6-dichloro-9,10-dihydroanthracene (**4c**) and 2,6-dimethoxycarbonyl-9,10-dihydroanthracene (**4d**) were not mentioned in the literature previously: For the synthesis of **4c** 2,6-dichloro-9,10-anthraquinone (**1c**) was employed as starting material, which was prepared as reported [9]. Reduction of the anthraquinone **1c** with aluminum and cy-

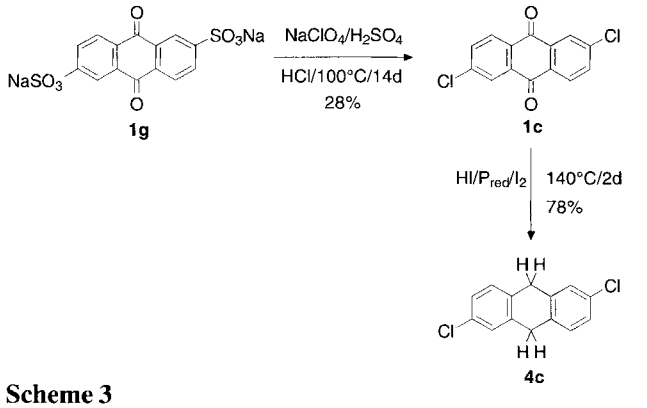


Scheme 1



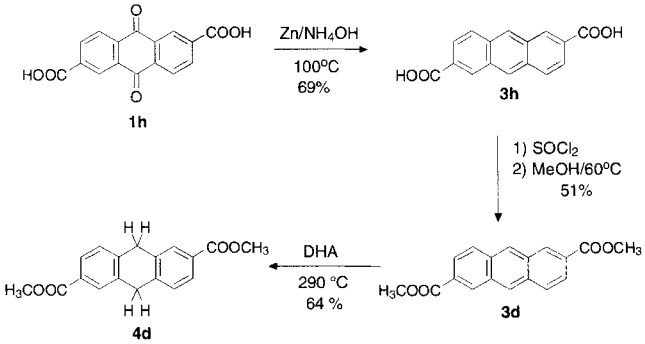
Scheme 2

clohexanol by a modified Meerwein-Ponndorf reduction [10] gave 2,6-dichloroanthracene in 40% yield, which, however, could not selectively be reduced to **4c**. Ultimately the 2,6-disubstituted anthraquinone **1c** was selectively reduced to **4c** by heating **1c** with an excess of concentrated hydroiodic acid and red phosphorus in a glass ampoule [11]. Under these conditions, pure **4c** was obtained in 78% yield.



Scheme 3

The synthesis of 2,6-dimethoxycarbonyl-9,10-dihydroanthracene (**4d**) started from 9,10-anthraquinone-2,6-dicarboxylic acid (**1h**), which was prepared by a literature procedure [12]. It was reduced with Zn/NH_4OH to 2,6-anthracenedicarboxylic acid (**3h**) and transformed into the diester **3d** by routine procedures. **3d** was successfully hydrogenated to 2,6-dimethoxycarbonyl-9,10-dihydroanthracene (**4d**) by transfer hydrogenation in a melt of DHA at 290 °C. Pure **4d** was obtained by chromatography on silica gel starting with *n*-hexane followed by diethyl ether and finally by crystallization from methanol.



Scheme 4

Results and Discussion

Samples of the acceptor α-methylstyrene (**5**) were heated to 290 – 350 °C in small ampoules under N_2 in diphenyl ether with a 10 fold excess of the 2,6-disubstitued 9,10-dihydroanthracenes **4a – d**. An almost quantitative yield of cumene (**6**) and of the corresponding 2,6-disubstituted anthracenes **3a – d** was determined by gc. The products were identified by comparison of their retention times with those of authentic samples and by gc-ms when required. As an example the mass balances of the transfer hydrogenations of α-methylstyrene (**5**) with 2,6-dimethoxy-9,10-dihydroanthracene **4a** (+M effect) and 2,6-dimethoxycarbonyl-9,10-dihydroanthra-

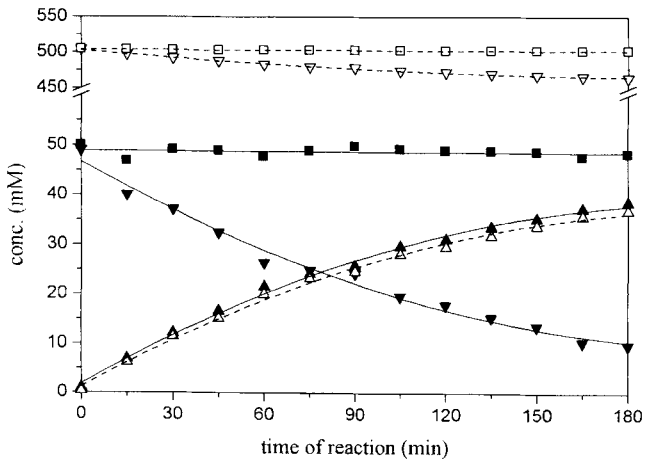


Fig. 1 Mass balance of the transfer hydrogenation of α-methylstyrene (5) (0.05M) by 2,6-dimethoxy-9,10-dihydroanthracene (**4a**) (0.50M) at 310 °C in diphenyl ether
▼ α–methylstyrene (**5**) ▲ cumene (**6**) ■ mass balance (**5** and **6**) ▽ 2,6-dimethoxy-9,10-dihydroanthracene (**4d**) △ 2,6-dimethoxyanthracene (**3a**) □ mass balance (**3a** and **4a**)

cene **4d** (–M effect), respectively, are shown in Figure 1 and Figure 2 (see also Experimental and references cited).

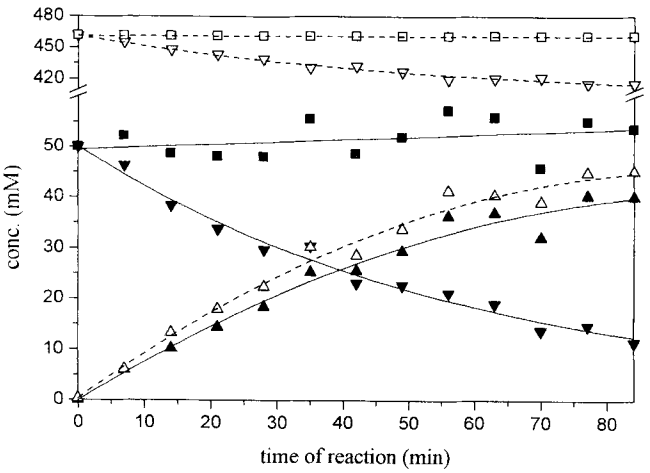


Fig. 2 Mass balance of the transfer hydrogenation of α-methylstyrene (5) (0.05M) by 2,6-dimethoxycarbonyl-9,10-dihydroanthracene (**4a**) (0.46M) at 320 °C in diphenyl ether ▼ α–methylstyrene (**5**) ▲ cumene (**6**) ■ mass balance **5** and **6**) ▽ 2,6-dimethoxy-9,10-dihydroanthracene (**4d**) △ 2,6-dimethoxyanthracene (**3d**) □ mass balance (**3d** and **4d**)

The reaction orders for the transfer hydrogenation of α-methylstyrene (**5**) with varying excess of the dihydroanthracenes **4a–d** were determined in diphenyl ether. In all cases the reactions followed pseudo first order kinetics. For an example the determination of the reaction order for the transfer hydrogenation of α-methylstyrene (**5**) (0.05M) with varying concentrations of 2,6-dimethoxy-9,10-dihydroanthracene (**4a**) at 320 °C is shown in Table 2 in the Experimental. Plotting the logarithm of k_{obs} versus the logarithm of [**4a**] the reaction order of **4a** was found to be 1.0 which is strong evidence for the retrodisproportionation being the first step of the reaction.

When the 2,6-disubstituted [9,10-D_4]-dihydroanthracenes were used, in no experiment incorporation of deuterium into **5** was detected (gc-ms) when the reaction was >70% complete. This is conclusive evidence that the retrodisproportionation step is irreversible under the reaction conditions and, therefore, rate-determining. The kinetic isotope effects k_H/k_D in Table 1 lie close to the maximum expected value [22] for the high reaction temperature of the kinetic experiments. The spread of k_H/k_D within the series of the donors seems to be mostly due to the varying temperatures.

It can also be seen from Table 1 that the change of solvent polarity has no significant influence on the rate constants k_2. The solvent effects for **4a** (0.9) and **4b** (1.1) in *N*-methylacetamide and **4c** (1.1) and **4d** (1.2) in benzonitrile (Table 1), respectively, are definitely too small to support an initial hydride- or electron-transfer. The almost identical free enthalpies of activation $DG^{\neq}_{300}$, enthalpies of activation $\Delta H^{\neq}$ and entropies of activation $\Delta S^{\neq}$ within the series **4a–d** (see Table 1) also exclude ionic intermediates and favor the H-atom transfer shown in Scheme 1. The four H-donors **4a–d** are useful new probes for distinguishing between ionic and free radical mechanisms of other H-transfer reactions.

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Experimental

The analytic instrumentation used in this investigation was described previously [6]. α-Methylstyrene (**5**) was available from previous work. Diphenyl ether (99.9%), *N*-methylacetamide (98.9%) and benzonitrile (99.9%) were purchased from Aldrich and thoroughly degassed with nitrogen (99.995%). The kinetic procedures and the product analyses by gc and gc-ms combination were also described previously and are reported in detail in ref. [13].

2,6-Dimethoxy-9,10-anthraquinone (**1a**)

A stirred suspension of 40.0 g (0.29 mol) carefully dried K_2CO_3 and 70 ml (0.42 mol) of dimethyl sulfate in 1.1 l acetone

Table 1 Activation parameters, isotope and solvent effects for the transfer hydrogenations of α-methylstyrene (**5**) (0.05M) with 2,6-dimethoxy-9,10-dihydroanthracene (**4a**) (0.50M), 2,6-bis(dimethylamino)-9,10-dihydroanthracene (**4b**) (0.50M), 2,6-dichloro-9,10-dihydroanthracene (**4c**) (0.51M) and 2,6-dimethoxycarbonyl-9,10-dihydroanthracene (**4d**) (0.46M) in diphenyl ether in the temperature range of 290–350 °C.

H-donor	$k_2 10^5$ [a] (M^{-1} s^{-1})	$\Delta G^{\neq}_{300}$ (kcal/mol)	$\Delta H^{\neq}$	$\Delta S^{\neq}$ (cal/mol K)	k_H/k_D	solvent effect [b]
4a	41.49 (3.1)	43.8±0.6	31.4±0.5	–21.7±0.8	$2.0_{330°C}$	0.9 [c]
4b	57.10 (0.8)	43.3±0.8	29.8±0.5	–23.5±0.9	$1.6_{340°C}$	1.1 [c]
4c	33.71 (1.7)	43.9±2.3	27.5±1.5	–28.5±0.9	$1.4_{350°C}$	1.1 [d]
4d	58.88 (3.7)	43.4±2.9	28.5±2.0	–26.0±3.7	$1.7_{310°C}$	1.2 [d]

[a] Rate constants k_2 at 310 °C; corrected for volume expansion at the reaction temperature and for the mean concentration of the H-donor during the hydrogenation process (number in parenthesis is % standard deviation); [b] $k_{solvent}/k_{DPE}$; the reference k_{DPE} is k_2 obtained in diphenyl ether ($\varepsilon_{30°C} = 3.7$ [20a]); [c] Solvent *N*-methylacetamide ($\varepsilon_{310°C} = 168.5$ [21]); [d] Solvent benzonitrile ($\varepsilon_{25°C} = 25.2$ [20b])

and of 6.0 g (25.0 mmol) 2,6-dihydroxy-9,10-anthraquinone was refluxed (oil bath: 100 °C) for 5 h under N_2. The warm reaction mixture was poured onto ice, and the acetone was removed by distillation. The solid product was filtered and dried. It was dissolved in 800 ml of boiling toluene and filtered. The brown filtrate was concentrated and kept at 5 °C overnight. Renewed recrystallisation from toluene afforded the pure quinone **1c** as yellow needles: 4.1 g (15.3 mmol, 61%), *m.p.* 259–266 °C (ref. [14]: 257 °C). – IR (KBr): ν/cm^{-1} = 1664, 1585, 1318, 1235, 1162, 1085, 1029, 985, 881, 751, 557. – ^{1}H NMR (250 MHz, $CDCl_3$): δ/ppm = 3.99 (s, 6H, $OC\underline{H}_3$), 7.24 (dd, J_1 = 2.7 Hz, J_2 = 8.8 Hz, 2H, 3,7-H), 7.73 (d, J = 2.7 Hz, 2H, 1,5-H), 8.24 (d, J = 8.6 Hz, 2H, 4,8-H).

$C_{16}H_{12}O_4$	Calcd.:	C 71.64	H 4.51
(268.3)	Found:	C 71.38	H 4.48.

2,6-Dimethoxy-9-anthrone (**2a**)

A stirred suspension of 3.5 g (13.1 mmol) 2,6-dimethoxy-9,10-anthraquinone (**1a**) and 2.6 g zinc dust in a mixture of 100 ml of NH_4OH (25%), 100 ml water and 100 ml ethanol was refluxed till the deep red suspension became yellow (2 h). After cooling to room temperature, the reaction mixture was poured on ice. Then 80 ml of concentrated HCl was added to dissolve the zinc. Filtration and drying afforded pale yellow needles of analytical pure anthrone **2a**: 3.1 g (12,2 mmol, 93%), *m.p.* 134–139 °C. – IR (KBr): ν/cm^{-1} = 1647, 1598, 1493, 1337, 1302, 1278, 1251, 1241, 1209, 1103, 1043, 778. – ^{1}H NMR (250 MHz, $CDCl_3$): δ/ppm = 3.92 (s, 6H, OCH_3), 4.27 (s, 2H, -CH_2-), 6.91 (d, J = 2.7 Hz, 1H, 5-H), 7.01 (dd, J_1 = 2.7 Hz, J_2 = 8.8 Hz, 1H, 7-H), 7.17 (dd, J_1 = 2.7 Hz, J_2 = 8.6 Hz, 1H, 3-H), 7.36 (d, J = 8.5 Hz, 1H, 4-H), 7.83 (d, J = 2.7 Hz, 1H, 1-H), 8.33 (d, J = 8,8 Hz, 1H, 8-H).

2,6-Dimethoxyanthracene (**3a**)

To a cold (0 °C) suspension of 190 mg (5.0 mmol) $LiAlH_4$ in 50 ml diethyl ether 500 mg (2.0 mmol) of anthrone **2a** was slowly added, and the mixture was stirred under an inert atmosphere for 1.5 h. It was then poured on ice and 80 ml of 2N HCl was added. The product was extracted several times with CH_2Cl_2. The combined organic phases were washed with a solution of Na_2CO_3 (10%), and with H_2O and dried with Na_2SO_4. The solvent was removed to give a solid crude product, which was recrystallized from toluene; yield of **3a**: 402 mg (1.7 mmol, 84%); *m.p.* 254–258 °C (ref. [15]: 257 °C). – IR (KBr): ν/cm^{-1} = 1630, 1478, 1437, 1352, 1302, 1216, 1184, 1152, 1136, 1033, 893, 809. – ^{1}H NMR (250 MHz, $CDCl_3$): δ/ppm = 3.95 (s, 6H, OCH_3), 7.15 (dd, J_1 = 2.4 Hz, J_2 = 8.8 Hz, 2H, 3,7-H), 7.16 (d, J = 2.4 Hz, 2H, 1,5-H), 7.84 (d, J = 8.8 Hz, 2H, 4,8-H), 8.20 (s, 2H, 9,10-H).

2,6-Dimethoxy-9,10-dihydroanthracene (**4a**)

To 100 ml of a 1:1-mixture of ethanol and toluene 500 mg (2.1 mmol) of **3a** was added under an inert atmosphere. 5.0 g (0.22 mol) of sodium was slowly added, and the mixture was refluxed for 4 h with stirring. After cooling to room temperature the solution was poured into water and the white precipitate was extracted several times with diethyl ether. The combined organic layers were dried with Na_2SO_4. Removal of the solvent and recrystallisation from ethanol under an inert atmosphere afforded **4a** as white plates: 280 mg (1.2 mmol, 56%); *m.p.* 126–130 °C (ref. [8]: 254–258 °C). – IR (KBr): ν/cm^{-1} = 1610, 1499, 1456, 1325, 1241, 1159, 1114, 1039, 936, 915, 820. – ^{1}H NMR (250 MHz, $CDCl_3$): δ/ppm = 3.80 (s, 6H, OCH_3), 3.86 (s, 4H, 9,9',10,10'-H), 6.74 (dd, J_1 = 2.4 Hz, J_2 = 7.9 Hz, 2H, 3,7-H), 6.84(d, J = 2.4 Hz, 2H, 1,5-H), 7.18 (d, J = 8.2 Hz, 2H, 4,8-H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm = 35.56, 55.44, 111.74, 112.92, 128.25, 128.58, 138.27, 158.16.

$C_{16}H_{16}O_2$	Calcd.:	C 79.97	H 6.71
(240.3)	Found:	C 79.86	H 6.66.

2,6-Bis(dimethyl)amino-9,10-anthraquinone (**1b**) [16]

To 300 ml trimethyl phosphate 20.0 g (84.0 mmol) of commercially available **1f** was added and the mixture was heated (oil bath: 205 °C) for 45 min. After cooling to room temperature a solution of 10.0 g (250 mmol) NaOH in 300 ml H_2O was added, and the reaction mixture was refluxed for 1 h. After cooling overnight the precipitate was filtered and washed several times with H_2O and air-dried. The solid was suspended in 1.5 l CH_2Cl_2, stirred for 1 h and filtered through 30.0 g silica gel. The deep red solution was concentrated, and after 2 d the precipitated needles were filtered: 8.5 g (28.9 mmol, 34%) orange needles **1b**; *m.p.* 320–325 °C (ref. [9]: 289 °C). – IR (KBr): ν/cm^{-1} = 1653, 1577, 1513, 1371, 1338, 1306, 1233, 1201, 1084, 932, 877, 821, 751. – ^{1}H NMR (250 MHz, $CDCl_3$): δ/ppm = 3.16 (s, 12H, $N(CH_3)_2$), 6.87 (dd, J_1 = 8.8 Hz, J_2 = 3.0 Hz, 2H, 3,7-H), 7.47 (d, J = 2.7 Hz, 2H, 1,5-H), 8.14 (d, J = 8.8 Hz, 2H, 4,8-H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm = 40.20, 109.85, 114.72, 122.39, 129.54, 135.93, 153.89, 182.67.

$C_{18}H_{18}N_2O_2$	Calcd.:	C 73.45	H 6.16	N 9.26
(294.4)	Found:	C 73.24	H 6.05	N 9.32.

2,6-Bis(dimethylamino)-9-anthrone (**2b**)

To a stirred solution of 12.0 g (300 mmol) NaOH in 120 ml H_2O, 8.0 g (27.2 mmol) of 2,6-bis(dimethylamino)-9,10-anthraquinone (**1b**) and 4.0 g of zinc dust was added. The reaction mixture was refluxed, and every 0.5 h further 4.0 g of zinc dust was added (overall 16.0 g). The suspension was heated for 24 h. After cooling to room temperature, the reaction mixture was poured in 800 ml H_2O, and the precipitate was filtered and dried. The solid was suspended in 1,5 l acetone, stirred for 1 h and filtered. The orange solution was concentrated and kept at 5 °C overnight for crystallization. Filtration and drying afforded anthrone **2b**: 4.5 g (16.1 mmol, 59%), *m.p.* 199–206°C. – IR (KBr): ν/cm^{-1} = 2872, 2802, 1645, 1593, 1507, 1358, 1306, 1228, 1207, 1181, 1098, 1064, 931, 860, 826, 771, 711, 579. – ^{1}H NMR (250 MHz, $CDCl_3$): δ/ppm = 3.02 (s, 6H, CH_3), 3.08 (s, 6H, CH_3), 4.18 (s, 2H, 9,9'-H), 6.57 (d, J =2.7 Hz, 1H), 6.76 (dd, J_1 = 2.7 Hz, J_2 = 8.8 Hz, 1H), 7.05 (d, broad, J = 7 Hz, 1H), 7.29 (d, J = 8.5 Hz, 1H), 7.69 (d, J = 3 Hz, 1H), 8.25 (d, J = 9 Hz, 1H). No simple assignment is possible, probably due to tautomerism.

2,6-Bis(dimethylamino)anthracene (**3b**)

Anthrone **2b** (3.0 g, 10. 7 mmol) and $LiAlH_4$ (3.5 g, 105.4 mmol) were allowed to react in 300 ml diethyl ether as de-

scribed for **2a**, with the exception, that 300 ml of concentrated NaOH solution was added after pouring the reaction mixture on ice. Recrystallisation from toluene afforded brown crystals of **3b**: 2.0 g (7.6 mmol, 71%); *m.p.* 238–242 °C (ref. [17]: 253–254 °C). – IR (KBr): ν/cm^{-1} = 1625, 1493, 1437, 1361, 1331, 1277, 1234, 1148, 973, 885, 794. – ^{1}H NMR (250 MHz, $CDCl_3$): δ/ppm = 3.05 (s, 12H, $N(CH_3)_2$), 7.02 (s, broad, 2H), 7.24 (m, J_1 = 9 Hz, 2H), 7.80 (d, J = 9.2 Hz, 2H), 8.07 (s, 2H, 9,10-H).

2,6-Bis(dimethylamino)-9,10-dihydroanthracene (**4b**)

To 200 ml 2-propanol 2.1 g (8.0 mmol) of **3b** was added under an inert atmosphere, and the mixture was refluxed. 31.0 g (1.35 mol) sodium and 170 ml ethanol was slowly added with stirring. The mixture was heated to such a temperature that the sodium melted. After all sodium was dissolved the hot solution was poured in cold water, and the white precipitate was extracted several times with diethyl ether. The combined organic layers were dried with Na_2SO_4. Removal of the solvent and recrystallization from methanol under N_2 afforded **4b** as white plates: 1.4 g (5.4 mmol, 68%); *m.p.* 131–132 °C. – IR (KBr): ν/cm^{-1} = 2934, 2863, 2788, 1615, 1565, 1500, 1424, 1343, 1225, 1165, 1114, 1058, 974, 840, 800, 580. – ^{1}H NMR (250 MHz, $CDCl_3$): δ/ppm = 2.91 (s, 12H, $N(CH_3)_2$), 3.84 (s, 4H, 9,9',10,10'-H), 6.62 (dd, J_1 = 2.7 Hz, J_2 = 8.2 Hz, 2H, 3,7-H), 6.70 (d, J = 2.7 Hz, 2H, 1,5-H), 7.14 (d, J = 8.2 Hz, 2H, 4,8-H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm = 35.56, 41.15, 111.20, 112.27, 125.34, 127.90, 137.89, 149.48.

$C_{18}H_{22}N_2$	Calcd.:	C 81.16	H 8.32 N 10.52
(266.4)	Found:	C 80.47	H 8.07 N 10.26.

2,6-Dichloroanthracene

A suspension of 2.5 g (92,7 mmol) aluminum, 50 mg $HgCl_2$, 50 ml cyclohexanol (freshly distilled from CaO) and 0,5 ml CCl_4 was refluxed for 20 h. To the gray suspension 4.0 g (14.8 mmol) of **1c** and 20 ml cyclohexanol were added, and refluxing was continued for 48 h. After cooling to room temperature the dark green mixture was poured into 250 ml H_2O, stirred for 1 h and carefully filtered. The filter cake was dissolved in toluene and dried with Na_2SO_4. Removal of the solvent and recrystallization from toluene afforded 2,6-dichloroanthracene as pale yellow plates: 1.4 g (5.7 mmol, 40%); *m.p.* 273–275 °C (ref. [18]: 271–272 °C). – IR (KBr): ν/cm^{-1} = 1610, 1445, 1076, 1063, 931, 906, 805.

$C_{14}H_8Cl_2$	Calcd.:	C 68.05	H 3.26
(247.1)	Found:	C 67.77	H 3.25.

2,6-Dichloro-9,10-dihydroanthracene (**4c**)

In a sealed glass ampoule (ID: 4.0 cm) 4.0 g (14.4 mmol) of **1c**, 4.2 g red phosphorus, 1.0 g iodine and 50 ml HI (57%) were heated (140 °C) for 72 h. After cooling to room temperature, the red precipitate was filtered and several times washed with hot water. It was dissolved in CH_2Cl_2 and the organic layer was dried with Na_2SO_4. The solvent was removed to give a solid crude product which was recrystallized from ethanol: 2.8 g (11.2 mmol, 78%) white needles of **3**; *m.p.* 143–145 °C. – IR (KBr): ν/cm^{-1} =2937, 2858, 2810, 1599, 1475, 1418, 1401, 1267, 1178, 1128, 1089, 958, 915, 894, 878, 810, 740, 709, 586, 547. – ^{1}H NMR (250 MHz, $CDCl_3$): δ/ppm = 3.94 (s, 4H, 9,10-H), 7.22 (dd, J_1 = 2.4 Hz, J_2 = 7.9 Hz, 2H, 3,7-H), 7.33 (d, J = 7.9 Hz, 2H, 4,8-H), 7.36 (d, J = 2.4 Hz, 2H, 1,5-H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm = 35.28, 126.35, 127.41, 128.64, 131.92, 134.25, 138.02.

$C_{14}H_{10}Cl_2$	Calcd.:	C 67.49	H 4.05
(249.2)	Found:	C 67.55	H 4.02.

2,6-Dimethoxycarbonyl-9,10-dihydroanthracene (**4d**)

In sealed glass ampoules (ID: 0.5 cm) a finely powdered mixture of 1.2 g (4.1 mmol) **3d** and 4.8 g (26.6 mmol) 9,10-dihydroanthracene was heated in a tin melt (290 °C) for 3.5 h. The ampoules were crushed, and the organic residue was dissolved in 1 l warm *n*-hexane. The suspension was filtered to separate not reacted **3d**. The filtrate was again filtered through 200 g silica gel whereby polar **4d** remained on the silica gel. Subsequent washing with diethyl ether, removal of the solvent and recrystallization from methanol afforded **4d** as pale yellow needles: 781 mg (2.6 mmol, 64%); *m.p.* 141–143 °C. – IR (KBr): ν/cm^{-1} = 2951, 1720, 1432, 1300, 1268, 1201, 1175, 1131, 1101, 981, 766, 745. – ^{1}H NMR (250 MHz, $CDCl_3$): δ/ppm = 9.92 (s, 6H, OCH_3), 4.03 (s, 4H, 9,10-H), 7.37 (d, J = 7.63 Hz, 2H, 4,8-H), 7.89 (dd, J_1 = 1.8 Hz, J_2 = 7.64 Hz, 2H, 3,7-H), 7.99 (d, J = 1.8 Hz, 2H, 1,5-H). – ^{13}C NMR (100MHz, $CDCl_3$): δ/ppm = 36.17, 52.05, 127.56, 128.43, 128.68, 136.06, 141.52, 167.11.

$C_{18}H_{16}O_4$	Calcd.:	C 72.96	H 5.44
(296.3)	Found:	C 72.57	H 5.22.

[9,9',10,10'-D_4]-9,10-Dihydroanthracenes (General procedure)

To a solution of 200 mg sodium in 20 ml ethanol-[D] (for **4d**: methanol-[D]) 500 mg of the substituted dihydroanthracenes **4a–d** was added. The mixture was refluxed for 3–5 d and then quenched by adding 20 ml D_2O, and the crude product was filtered. Sublimation afforded the deuterated derivatives in high analytical purity and nearly quantitative yield. The amount of deuterium incorporated was determined by ^{1}H NMR.

Kinetics

The method for carrying out the kinetic measurements was described previously [2] and reported in detail in ref. [13]. The kinetics were followed under pseudo-first-order conditions (k_{obs}) using a 9 to 10 fold excess of H-donor. The rate constants k_2 were calculated from k_{obs} and from the amount of conversion of the H-donor at the related reaction time. The conversion was estimated from the thermal expansion of the diphenyl ether/H-donor mixture [19a] and the concentration of the H-donor after half of the respective reaction time [19b]. The rate constants of the transfer hydrogenations of **5** by **4a–d** and the corresponding deuterated compounds, respectively, in diphenyl ether were determined over a temperature range of 40 K for calculating the activation parameters. – Determination of the reaction order: Solutions of α-methylstyrene (**5**) (0.05M), *n*-dodecane (0.05M, internal standard) and varying concentrations of **4a–d** (as example the concentrations of **4a** are shown Table 1) in diphenyl ether were heated in order to

determine the dependence of k_{obs} on the concentration of the H-donor.

Table 2 Determination of the reaction order: Pseudo first order rate constants k_{obs} for the transfer hydrogenation of α-methylstyrene (**5**) (0.05M) by varying concentrations of 2,6-dimethoxy-9,10-dihydroanthracene (**4a**) in diphenyl ether at 320 °C.

temperature [a] (°C)	time [b] (min)	$[\mathbf{4a}]_M$ [c] (M)	$k_{obs}10^5$ (σ^{-1})	s (%)
320.3	220	0.298	12.65	1.8
320.2	180	0.473	21.45	1.2
320.0	120	0.751	35.24	1.5
320.1	80	0.973	40.18	1.7

[a]) Standard deviation ± 0.2 °C; [b]) Time of reaction; [c]) Mean concentration of the H-donor (concentration of **4a** after one half of the respective reaction time)

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