Bimolecular Formation of Radicals by H-Transfer, 6[1]

Uncatalyzed Transfer Hydrogenation of a Benzhydryl Fluoride by 9,10-Dihydroanthracene

Frank Schaffer, Hans-Dieter Beckhaus, Hans-Jürgen Rieger, and Christoph Rüchardt*

Institut für Organische Chemie und Biochemie der Universität Freiburg,
Albertstraße 21, D-79104 Freiburg i.Br.

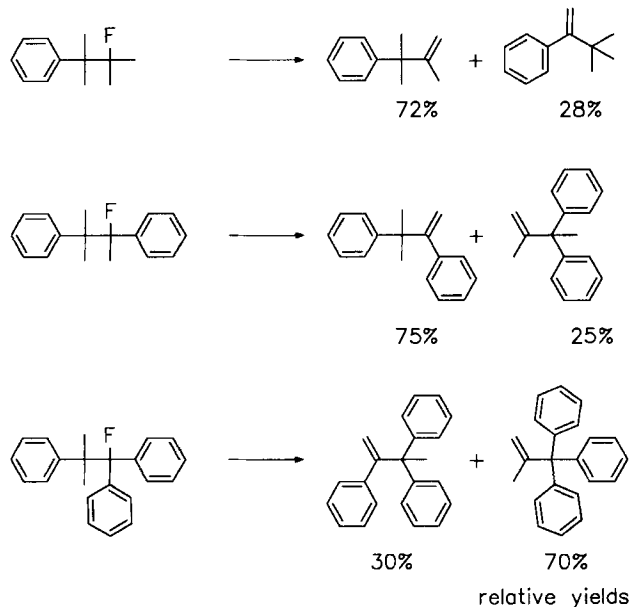1-Adamantylfluorodiphenylmethane (**2**) was reduced to 1-adamantyldiphenylmethane (**3**) when heated with 9,10-dihydroanthracene to 330°C. From the second-order kinetics, the activation parameters ($\Delta H^{\neq}$ = 37.2 ± 0.5 kcal mol^{-1}, $\Delta S^{\neq}$ = −18.8 ± 0.8 cal mol^{-1} K^{-1}), the kinetic isotope effect k_H/k_D = 2.4 (373°C)[17], and the observation of intermediate radical species by ESR it was concluded that the reaction is a new example of a molecule-induced radical formation (MIRF) process. This is supported by thermochemical data.

In the course of the investigation of substituent effects on the CC-bond cleavage reaction[2] we became interested in the influence of α-fluorine substitution. The selected model compounds, however, either did not react at all when heated to 300°C (e.g. 1,1,2,2-tetrafluoro-1,2-diphenylethane, 1,1,1-trifluoro-2,2,2-triphenylethane, 1,1,1-trifluoro-2,2-diphenylethane) or reacted with elimination of HF, even at lower temperatures, partly associated with carbon skeletal rearrangements.

Scheme 1. HF elimination by thermolysis at 220°C in mesitylene

We therefore prepared 1-adamantylfluorodiphenylmethane (**2**) from the corresponding carbinol **1**[3] and (diethyl-amino)sulfur trifluoride (DAST)[4] in 70% yield and purified it by crystallization from ethanol to 99.99% purity.
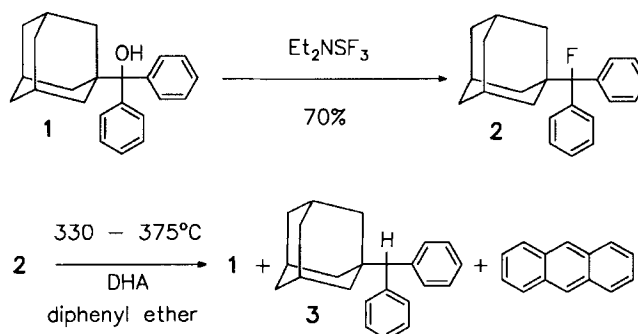
We expected that cleavage of the C−C bond between the 1-adamantyl group and the fluorodiphenylmethyl group would be the dominating path in a thermolysis reaction. When **2** was heated to temperatures between 330 and 375°C in diphenyl ether or mesitylene under nitrogen with added 9,10-dihydroanthracene (DHA) as a radical scavenger in a ten molar excess, 1-adamantyldiphenylmethanol (**1**), 1-adamantyldiphenylmethane (**3**), anthracene, and HF were obtained as reaction products in not well reproducible yields.

No C−C cleavage products were detected. Because we suspected the reaction of HF with the glass surface to be a source of H$_2$O, which could hydrolyze **2** to **1**, possibly catalyzed by HF[5], we used 1-(trimethylsilyloxy)-1-cyclohexene as solvent and efficient trap of HF. Under these reaction conditions no alcohol **1** was formed, and a ≥95% yield of 1-adamantyldiphenylmethane (**3**) was obtained besides anthracene, cyclohexanone, and trimethylsilyl fluoride. In con-

trol experiments either without DHA or without the fluoride **2** no reaction occurred.
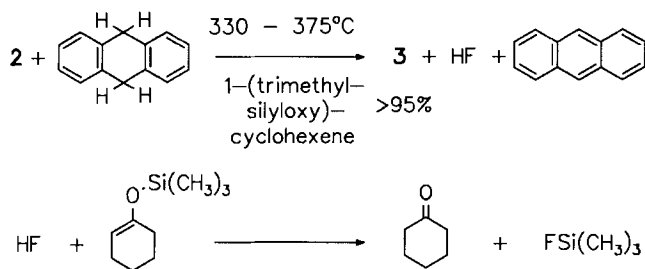
In analogy to the transfer hydrogenations of alkenes recently described[1,6], we suggested for this new reaction type the homolytic non-chain mechanism formulated in Scheme 2.

Scheme 2
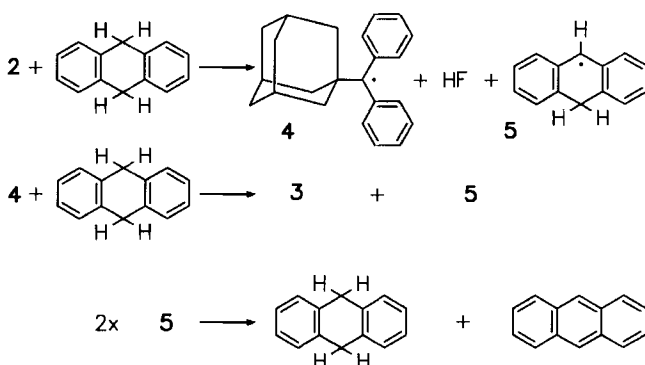
The first step of this sequence is without precedent[7] and represents a new type of molecule-induced homolysis reaction, while the second and third step are routine hydrogen transfer and disproportionation steps. To test this proposal, the mechanism of this reaction was investigated in more detail.

Identification of Radicals by ESR

When the reaction was performed in the cavity of an ESR spectrometer, neither the known spectrum of the 9-hydroanthryl radicals[8] (**5**) nor that of the 1-adamantyldiphenylmethyl radicals (**4**) was detected. When xanthene (**6**) was used instead of DHA as a hydrogen source at 277°C in diphenyl ether, an intense well-resolved spectrum characteristic of 9-xanthyl radicals (**7**) could be recorded. When 7*H*-benzanthrene (**8**) was used as H donor in 1-(trimethylsilyloxy)-1-cyclohexene at 200°C, there was observed also a highly resolved spectrum, which was identical with the spectrum of the 7-benzanthryl radicals (**9**) obtained by heating of **8** with di-*tert*-butyl hyponitrite[9a,b] (Figure 1) and which could be simulated by using the coupling constants given in the literature[9c]. Radicals **7** and **9** are built up in higher concentrations because they cannot disappear in a fast dis-
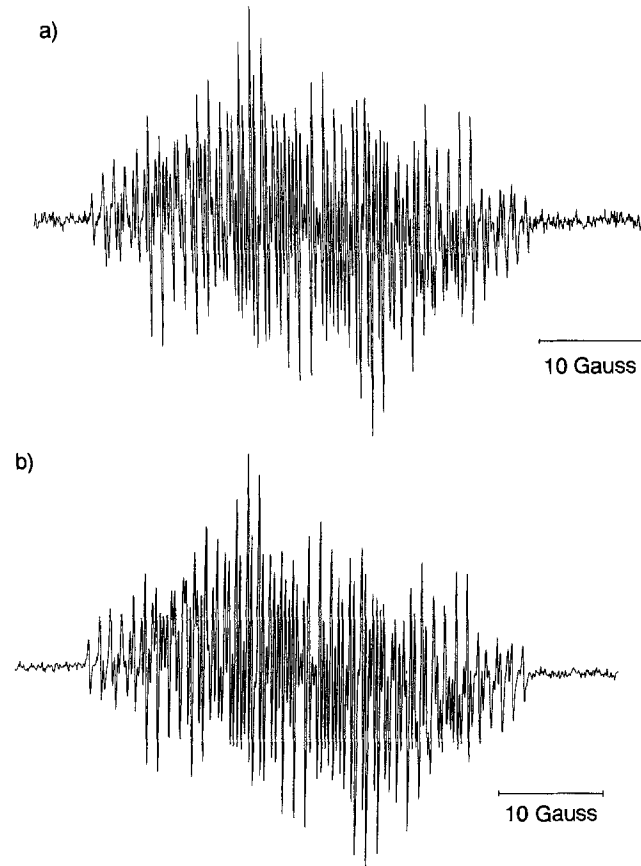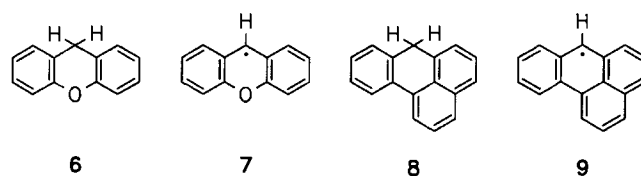

Figure 1. ESR spectra of 7-benzanthryl radicals (**9**) a) generated by hydrogen transfer reaction of 7*H*-benzanthrene (**8**) with **2** at 200°C; b) by heating of **8** with di-*tert*-butyl hyponitrite at 200°C (for experimental conditions, see experimental part)

proportionation reaction as the 9-hydroanthryl radicals do.

Under no circumstances, e.g. heating of **2** in 1-(trimethylsilyloxy)-1-cyclohexene without a H donor, was the spectrum of 1-adamantyldiphenylmethyl radicals (**4**) found. For comparison, this spectrum was generated and recorded by heating 1-adamantylchlorodiphenylmethane with copper powder in benzene (Figure 2a).

The spectrum was simulated by choosing appropriate coupling constants from the known spectra of diphenylmethyl radicals[10] and 1-adamantyl-substituted methyl radicals[11] (Figure 2b). The structure of the radical was calculated with the MM2 force field[12] and found to be similar to the structure of the *tert*-butyldiphenylmethyl radical whose ESR spectrum had been analyzed previously[13]. By using INDO calculations[14] on these MM2 structures it was possible to show that the spin density of the aromatic protons in the 1-adamantyldiphenylmethyl
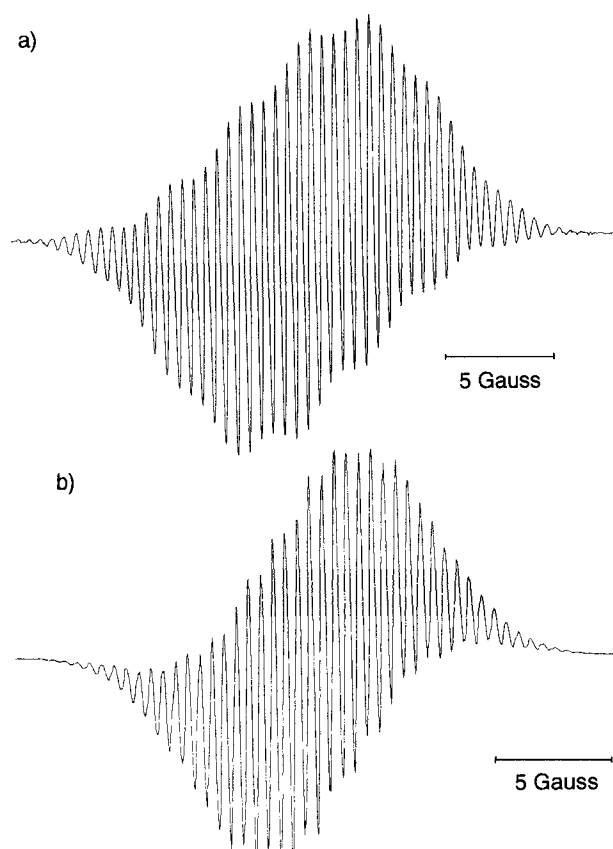
a)

5 Gauss

b)

5 Gauss

Figure 2. ESR spectrum of 1-adamantyldiphenylmethyl radicals (4) a) generated by heating of 1-adamantylchlorodiphenylmethane and copper powder (for experimental conditions, see experimental part); b) simulated spectrum

Table 1. Kinetics of the H-transfer reaction of 1-adamantylfluorodiphenylmethane (2) (0.02 mol l^{-1}) with added hydrogen donors in 1-(trimethylsilyloxy)-1-cyclohexene

T [°C]	H donor	c[a]	10^4·k$_{ps}$[b]	10^4·k$_2$[c]	σ [%]	yield [%]
375.0	DHA[d]	0.5	1.38	2.75	3	96
375.0	-	-	-	2.82[e]	-	-
373.3	DHA	2.0	5.19	2.65	8	99
373.6	DHA	-	-	2.65[e]	-	-
371.8	DHA	-	-	2.45[e]	-	-
363.9	DHA	1.9	3.45	1.74	7	96
356.2	DHA	1.9	2.23	1.15	18	95
353.7	DHA	-	-	1.03[e]	-	-
343.5	DHA	2.0	1.21	0.61	11	94
331.8	DHA	1.7	0.67	0.39	1	98
373.6	[D$_4$]DHA[f]	2.0	2.23	1.12	7	94
371.8	6[g]	2.0	6.93	3.50	13	96
353.7	8[h]	0.8	4.84	6.16	20	99

[a] Concentration of the H donor in mol l^{-1}. – [b] Observed pseudo-first-order rate constant k_{ps} in s^{-1}. – [c] Second order rate constant k_2 in l mol^{-1} s^{-1} derived from k_{ps}. – [d] CH bond dissociation enthalpy of DHA BDE = 78 kcal mol^{-1}[16]. – [e] Extrapolated values of k_2 for comparison of different H donors. – [f] See ref.[17]. – [g] CH bond dissociation enthalpy of 6 BDE = 75.5 kcal mol^{-1}[16]. – [h] CH bond dissociation enthalpy of 8 BDE = 66 kcal mol^{-1}[18].

Table 2. Activation parameters for the reaction of 2 with DHA

ΔH$^{\neq}$[a]	ΔG$^{\ddagger}_{(300°C)}$[a]	ΔS‡[b]
37.2 ± 0.5	48.0 ± 0.5	-18.8 ± 0.8

[a] In kcal mol^{-1}. – [b] In e.u.

Kinetics and Thermochemistry

radicals was very similar to that of the *tert*-butyldiphenylmethyl radicals.

The rates of this reaction were followed under nitrogen at temperatures between 330 and 375°C[15] in 1-(trimethylsilyloxy)-1-cyclohexene by using the ampoule technique and GC analysis. The H donor was added in at least tenfold excess to provide pseudo-unimolecular conditions.

Second-order rate constants k_2 were calculated by dividing the pseudo-unimolecular constants k_{ps} by the H-donor concentration (Table 1). The activation parameters ΔH$^{\neq}$ and ΔS$^{\neq}$ were calculated from the temperature dependence of these DHA transfer rates (Table 2).

The entropy of activation is close to the corresponding value for the uncatalyzed H-transfer reaction from DHA to α-methylstyrene[6a] and supports the existence of a bimolecular collision complex in the transition state.

Of great interest is the question how the enthalpy of activation ΔH$^{\neq}$ compares with the enthalpy of reaction ΔH$_R$ of the H-transfer step. For this purpose, the enthalpy of formation of 1-adamantylfluorodiphenylmethane (2) was deduced from the heat of combustion ΔH^0_C(c) 2 = −3001.43 ± 0.45 kcal mol^{-1}, measured in a calorimeter equipped with a rotating bomb, and from the heat of subli-

mation ΔH$_{sub}$ 2 = 30.1 ± 0.3 kcal mol^{-1}, determined from the temperature dependence of the vapor pressure.

ΔH^0_f(g) 2 = −28.8 ± 0.6 kcal mol^{-1} was obtained. This value was combined with data for the heat of formation of HF, DHA, 9-hydroanthryl radical (5) and anthracene from the literature[19a] and the calculated value (MM2)[12b] for 1-adamantyldiphenylmethane (3)[19b]. The heat of formation of 4 = 51.0 ± 1.0 kcal mol^{-1} was obtained as the sum of ΔH^0_f(g) 3 and the CH bond dissociation enthalpy of the latter. The BDE of 3 = 82.9 ± 1.0 kcal mol^{-1} was deduced from the measured RSE = 12.9 ± 0.9 kcal mol^{-1}[19c] of a diphenylmethyl radical combined with the BDE of isobutane (BDE = 95.8 ± 0.4 kcal mol^{-1}[19d]). From these values the enthalpy of reaction for the first step of the hydrogen transfer reaction (Scheme 3) and for the overall reaction sequence (Scheme 4) was obtained.

The close agreement between the enthalpy of activation of the molecule-induced H transfer (ΔH$^{\neq}$ = 37.2 ± 0.5 kcal mol^{-1}) and the enthalpy of reaction for the first step (ΔH$_R$ = 37.7 ± 2.2 kcal mol^{-1}) suggests that the transition state of this reaction is a late one and closely resembles that of the radicals. This was also observed for the H-transfer reactions of alkenes previously[1,6]. There, however, it was expected, because the reverse process, a radical disproportionation, is known to occur without an enthalpic activation barrier. The reverse process of the H transfer from DHA to 2, however, would have to be a termolecular process, which is kinetically unfavorable.

The kinetic isotope effects of the two H-transfer reactions are also similar, k_H/k_D = 2.1 (determined at 300°C) for the transfer from DHA to α-methylstyrene[6a] and k_H/k_D = 2.4 (determined at 373°C) for the new process, the transfer

B

Scheme 3. Enthalpy of reaction for the first step of the H-transfer reaction (all values in kcal mol^{-1})

2	+			
ΔH_f° -28.8 ± 0.6		38.2 ± 1.1		

4	+	HF	+	**5**
ΔH_f° 51.0 ± 1.0		-65.3 ± 0.2		61.4 ± 1.5
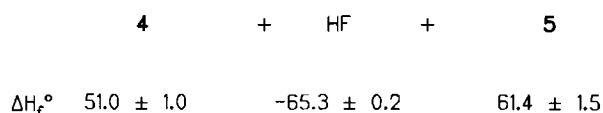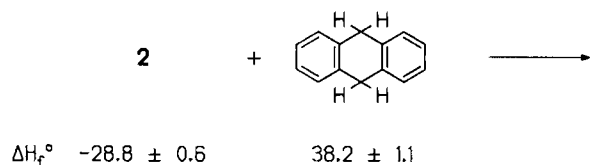
$$\Delta H_R = 37.7 ± 2.2$$

Scheme 4. Enthalpy of reaction for the overall reaction (all values in kcal mol^{-1})

2	+	
ΔH_f° -28.8 ± 0.6		38.2 ± 1.1

4	+	HF	+	
ΔH_f° 51.0 ± 1.0		-65.3 ± 0.2		55.2 ± 0.5
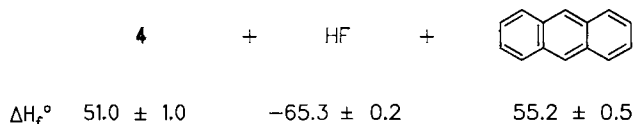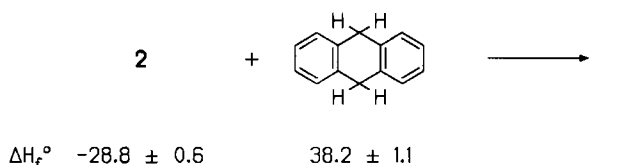
$$\Delta H_R = 0.7 ± 1.4$$

from [D$_4$]DHA[17] to **2**. From this reaction [D$_2$]anthracene, [D]cyclohexanone, and [D]-**3** were obtained as reaction products according to the proposed mechanism.

Despite the enthalpy $\Delta H_R = 0.7 ± 1.4$ kcal mol^{-1} for the total reaction (Scheme 4) it must not be expected that an equilibrium is reached. This situation is reminiscent of radical fragmentation processes like the concerted decomposition of azo compounds[20] or peresters[21].

The influence of the C$-$H bond strengths of the H donors on the rates also supports the molecule-induced hydrogen transfer as rate-determinating step. There exists a rough correlation between the C$-$H bond strengths and the rate constants of hydrogen transfer as expected (see Table 1).

Work is in progress to investigate the scope of this new elementary process for generating radicals. We have successfully observed H-transfer reactions of this type with 1-adamantylchlorodiphenylmethane, triphenylfluoromethane, diphenylfluoromethane, benzyl fluoride, 9-fluorenol[22], and several ketones of the benzophenone type[22], although not yet in optimized yields. The driving force for the hydrode-

fluorination reaction is undoubtedly the high bond strength of HF (136 kcal mol^{-1})[23]. The bond strength in H$_2$O (119 kcal mol^{-1})[23], however, seems to be also sufficient.

Experimental

^{1}H NMR: Bruker WM 250 (250 MHz), Bruker AM 400 (400 MHz); CDCl$_3$/TMS as internal standard. $-$ ^{13}C NMR: Bruker AM 400 (100 MHz); CDCl$_3$/TMS as internal standard. $-$ ^{19}F NMR: Bruker AC 200 (188 MHz); CDCl$_3$/CFCl$_3$ as internal standard. $-$ FT-IR: Nicolet Impact 400. $-$ Elemental analyses: Perkin-Elmer Elemental Analyser 240. $-$ GC: Carlo-Erba fractometer GC 6000, Vega Series 2 with FID, Carlo-Erba Autosampler CTC-A 200; capillary column SE 30/25 m with an inner diameter of 0.32 mm and a layer thickness of 0.25 µm; N$_2$ flow 2 ml min^{-1}; temperature program: 75°C (5 min isotherm), heating rate 10 K min^{-1}, 250°C (7.5 min isotherm). $-$ GC/MS: Varian fractometer 3700; Finnigan Mat 44s. $-$ DSC: Perkin-Elmer DSC-2. $-$ ESR: Bruker BER-420; field controller B-H15; microwave unit ER 048R. $-$ Melting points (uncorrected): Büchi melting point apparatus. $-$ Thermolysis: Tin thermostat (self-constructed)[24]; electronic temperature control unit Oxford Electronic Instruments DTC 2/CK 01; temperature measurement Systemtechnik AB Pt 100/S 1220.

Starting Materials: All compounds were handled under N$_2$ by using carefully dried glassware and solvents. 1-Adamantyldiphenyl-methanol[3] (**1**), 1-adamantylchlorodiphenylmethane[3], 1-adamantylmethoxydiphenylmethane[3], and 1-(trimethylsilyloxy)-1-cyclohexene[25] were prepared according to literature procedures and purified either by recrystallization or distillation until a purity of $\geq$99% was reached. 7*H*-Benzanthrene[26] was prepared by reduction of 25.0 g (0.1 mol) of benzanthrone with 7.2 g (0.19 mol) of LiAlH$_4$ and 56.1 g (0.38 mol) of AlCl$_3$ in 63% yield. [D$_4$]DHA[6b] was prepared by treatment of 6.00 g (33.4 mmol) of DHA with 3.26 g (144.8 mmol) of sodium in 60 ml of C$_2$H$_5$OD in 90% yield[17]. Di-*tert*-butyl hyponitrite[9a] was obtained by reaction of 4.8 g (35 mmol) of *tert*-butyl bromide with 0.6 g (3.7 mmol) of iron(III) chloride and 0.4 g (3.8 mmol) of sodium hyponitrite in 83% yield. The commercial products 9,10-dihydroanthracene (Fluka) and xanthene (Aldrich) were recrystallized from ethanol.

1-Adamantylfluorodiphenylmethane (**2**): A solution of 1.47 g (10 mmol) of (diethylamino)sulfur trifluoride[4] in 10 ml of dichloromethane was cooled to $-$80°C. To this solution 3.18 g (10 mmol) of 1-adamantyldiphenylmethanol (**1**) in 10 ml of dichloromethane was added. After the addition the mixture was allowed to warm up to room temp., then 20 ml of water was added. The organic layer was washed with 0.1 N sodium hydrogencarbonate solution and water. After drying with sodium sulfate, the solvent was evaporated and the crude product recrystallized from ethanol. Thus, **2** was obtained with 99.99% purity (DSC)[27]. Yield 2.23 g (70%), m.p. 132°C (ethanol). $-$ IR (CCl$_4$): $\tilde{v} = 1603$ cm^{-1} (aromatic ring), 1588 (aromatic ring), 1009 (CF), 984 (CF). $-$ ^{1}H NMR (250 MHz): $\delta = 1.53-1.68$ (m, 6H, CH$_2$, 1-H), 1.80 (s, 6H, CH$_2$, 3-H), 1.98 (s, 3H, CH, 2-H), 7.18$-$7.63 (m, 10H, aromatic H). $-$ ^{13}C NMR (100 MHz): $\delta = 28.66$ (s, C-2), 36.88 (s, C-1), 36.99 (d, $J = 5$ Hz, C-3), 41.54 (d, $J = 24$ Hz, C-4), 101.69 (d, $J = 181$ Hz, C-5), 126.87 (d, $J = 6$ Hz, C-7), 127.02 (s, C-9), 127.53 (d, $J = 2$ Hz, C-8), 141.84 (d, $J = 24$ Hz, C-6). $-$ ^{19}F NMR (188 MHz): $\delta = -158.29$ (s, CF). $-$ MS (70 eV), *m/z* (%): 320 (2) [M$^+$], 135 (100) [adamantyl]. $-$

HRMS: calcd. 320.19359; found 320.1936. — $C_{23}H_{25}F$ (320.6): calcd. C 86.19, H 7.88; found C 86.40, H 7.87.

2   **3**
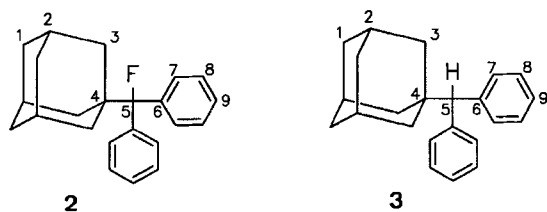
1-Adamantyldiphenylmethane (**3**): An alloy was prepared by heating 2.00 g (51.2 mmol) of potassium and 2.00 g (87.0 mmol) of sodium under N_2. 400 mg of this alloy (5.12 mmol K) was suspended in 10 ml of benzene and 770 mg (2.32 mmol) of 1-adamantylmethoxydiphenylmethane in 20 ml of benzene was added to the suspension. The mixture was heated under reflux for 2 h until the solution became dark-red. After cooling to room temp., 50 ml of methanol was added to destroy excess alloy. Then 50 ml of water was added, and the aqueous layer was extracted with ether. After drying of the extract with sodium sulfate and evaporation of the solvent the crude product was recrystallized from hexane. Yield 670 mg (95%), m.p. 104°C (hexane). — IR (CCl_4): $\tilde{v} = 1601$ cm^{-1} (aromatic ring), 1581 (aromatic ring). — ^1H NMR (400 MHz): $\delta =$ 1.80−2.05 (m, 12H, CH_2, 1-, 3-H), 2.25 (s, 3H, CH, 2-H), 3.81 (s, 1H, CH, 5-H), 7.41−7.81 (m, 10H, aromatic H). — ^{13}C NMR (100 MHz): $\delta = 28.85$ (s, C-2), 36.88 (s, C-1), 36.96 (s, C-3), 41.17 (s, C-4), 66.50 (s, C-5), 125.98 (s, C-8), 127.84 (s, C-9), 130.03 (s, C-7), 142.14 (s, C-6). — MS (70 eV), m/z (%): 302 (1) [M$^+$], 135 (100) [adamantyl]. — $C_{23}H_{26}$ (302.4): calcd. C 91.34, H 8.66; found C 91.16, H 8.61.

Kinetic Measurements: The rate constants of the transfer reaction of **2** with different H donors (concentrations see Table 1) were measured under pseudo-first-order conditions at constant temperature in 1-(trimethylsilyloxy)-1-cyclohexene as solvent and with *n*-tricosane as internal standard. According to the ampoule technique[24b] 0.1 ml of these solutions was filled in glass ampoules which had a total volume of 0.5 ml. After degassing of these ampoules, they were sealed under nitrogen. For thermolysis they were placed for different times into a tin thermostat at the temperatures indicated in Table 1. For the measurement of each value of k_{ps} 10−12 ampoules were heated until 70−90% conversion was reached, then they were analyzed by GC. The decrease of **2** and the increase of **3** were measured[24b]. In Table 3 are listed the concentrations of **2** and **3**, the sum of these concentrations, and the yield related to the used fluoride **2** for one measurement of k_{ps} at 363.9°C.

The rate constants for the H transfer k_2 were calculated from k_{ps} and the H-donor concentrations (see Table 1). The activation parameters were calculated from the temperature dependences of the rate constants k_2 by the Eyring correlation using statistical weigths[28] and are listed in Table 2.

Product Analyses by GC: For quantitative and qualitative product analyses the ampoules were thermolyzed until >90% conversion was reached. The products were qualitatively analyzed by GC by a comparison with authentic samples. For the quantitative analyses of the reaction products the area correction factors of all compounds were determined. The products were **3**, cyclohexanone, and anthracene. The latter two were detected in various yields, depending on the time of thermolysis but their yield was always higher than that of **3**, which was detected in >95% yield (related to the used **2**).

Table 3. Measurement of the rate constant for the reaction of **2** (23.60 mM) with DHA (1.94 M) in 1-(trimethylsilyloxy)-1-cyclohexene at 363.9°C

t [min][a]	3[b]	2[c]	2 + 3[d]	yield [%]
0	0.89	21.26	22.15	94
10	6.88	15.48	22.36	95
20	9.59	13.49	23.07	98
30	9.61	13.06	22.67	96
40	12.74	9.78	22.52	95
50	14.65	7.77	22.42	95
60	18.80	4.59	23.40	99
70	18.19	4.24	22.42	95
100	19.42	3.32	22.74	96
110	21.67	1.66	23.32	99

$$k_{ps} = 3.45 \cdot 10^{-4} \pm 2.4 \cdot 10^{-5}\ s^{-1}\ [e]$$
$$k_2 = 1.74 \cdot 10^{-4} \pm 1.2 \cdot 10^{-5}\ l\ mol^{-1}\ s^{-1}\ [f]$$

[a] Time of thermolysis, corrected by the heating phase (5 min). — [b] Concentration of **3** in mmol l^{-1}. — [c] Concentration of **2** in mmol l^{-1}. [d] Concentration of **2** and **3** in mmol l^{-1}. — [e] Observed pseudo-first-order rate constant k_{ps}. — [f] Second-order rate constant k_2 derived from k_{ps}.

When [D$_4$]DHA[17] was used as H donor, [D$_2$]anthracene, [D]cyclohexanone, and [D]-**3** were obtained as reaction products in >95% yield. When xanthene (**6**) was used as H donor 9,9'-bixanthene was obtained in >90% yield.

Heat of Combustion: For the measurement of the heat of combustion of **2** an isoperibolic macrocalorimeter[29] with a stirred water bath was used. The inner surface of the combustion bomb was totally coated with platinum, and the whole bomb could be rotated to dissolve the reaction gases in the bomb liquid (5 ml of water). The substance was pressed to a pellet, and the procedure was performed as described in ref.[30]. The heat equivalent of the calorimeter was calibrated with benzoic acid (sample SRM 39i, National Bureau of Standards) and checked with *p*-fluorobenzoic acid as a secondary reference compound ($\varepsilon_{calor} = 5996.18 \pm 0.52$ cal K^{-1}). The specific heat capacity of **2** $c_p = 0.28$ cal g^{-1} K^{-1} was measured with DSC. The density of **2** was determined to be $\rho = 1.25$ g cm^{-3}.

For the calculation of the isothermic bomb process and the correction of the data to standard conditions conventional procedures[31] were used. The results of the combustion experiments are listed in Table 4.

Enthalpy of Sublimation: The enthalpy of sublimation ΔH_{sub} of **2** was determined by transfer of **2**[32] in a saturated N_2 stream. The apparatus and the procedure used are described in ref.[30]. The vapor pressure *p* was deduced from the amount of substance which was condensed and measured by GC analysis using an internal standard. The vapor pressure of **2** at the condensation temperature was calculated by an iterative method[33]. The obtained data are given in Table 5.

From a linear regression of ln*p* against $1/T$ a value of $\Delta H_{sub} = 30.1 \pm 0.3$ kcal mol^{-1} was calculated.

Force-Field Calculations: Various conformations of the radicals were generated with the molecular modelling program Chem-X[34]. Optimization was performed with the force-field program MM2[12]. The force-field parameters for alkyl and benzyl radicals[12b] were used for these calculations.

ESR Measurements

9-Xanthyl Radicals (**7**): A solution of **2** (0.1 M) and **6** (1 M) in diphenyl ether was heated under N_2 to 277°C in the cavity of the ESR spectrometer. Spectrometer conditions: Magnetic strength in the middle of the spectrum 3326.9 G, modulation 0.32 G, amplifi-

Table 4. Heats of combustion of 1-adamantylfluorodiphenylmethane (2)

experiment number	1	2	3	4	5
m (2) [g][a]	0.311048	0.326868	0.292418	0.308608	0.332769
m_{cotton} [g][a]	0.000901	0.000835	0.000938	0.000626	0.000901
ΔT_c [K][b]	0.485991	0.510383	0.456665	0.481569	0.519931
$\varepsilon_{calor}(-\Delta T_c)$ [cal][c]	2914.09	3060.34	2738.24	2887.57	3117.60
$\varepsilon_{cont}(-\Delta T_c)$ [cal][c]	-3.45	-3.64	-3.24	-3.43	-3.71
ΔE_{corr} [cal][d]	2.30	2.42	2.15	2.27	2.46
$m_{cotton}\Delta u_c$ [cal][d]	3.60	3.34	3.75	2.50	3.60
Δu_c (2) [cal g⁻¹]	-9359.61	-9355.06	-9353.82	-9351.24	-9360.51
ΔH_c (2) [kcal mol⁻¹][e]	-3002.88	-3001.42	-3001.02	-3000.19	-3003.17
ΔH_f (2) [kcal mol⁻¹][e]	-57.51	-58.97	-59.37	-60.20	-57.23

[a] m: air-reduced masses. − [b] $\Delta T_c = T_f - T_i + \Delta T_{corr}$; $T_h = 25°C$; $V_{bomb} = 0.2664$ l; $p^i_{gas} = 30.00$ atm (30.40 bar); $m^i_{water} = 5$ g; $E_{ignit} = 0.35$ cal; $T_i = 24.5°C$; $m_{platinum} = 9.763$ g. − [c] $\varepsilon_{calor} = 5996.18 \pm 0.52$ cal/K (±0.0087%) from calibration measurements with benzoic acid; $\varepsilon_{cont}(-\Delta T_c) = \varepsilon^i_{cont}(T_i - 25°C) + \varepsilon^f_{cont}(25°C - T_f + \Delta T_{corr})$. − [d] ΔE_{corr}: sum of the items 81−85, 87−90, 93, and 94 given in ref.[31]; $-m_{cotton}\Delta u_c$: amounts of heat released by the combustion of the auxiliary compounds. − [e] Average from 5 measurements: ΔH_c (2) = −3001.74 ± 0.65 kcal mol⁻¹ (±0.027%); ΔH_f (2) = −58.66 ± 0.56 kcal mol⁻¹.

Table 5. Determination of the vapor pressure of 2 measured in a flow system[30,32]

T [°C][a]	2 [mg][b]	V [l][c]	p [Torr][d]
80	0.182	63.50	0.17·10⁻³
90	0.399	40.17	0.58·10⁻³
100	0.655	23.00	1.65·10⁻³
120	0.959	4.17	13.40·10⁻³

[a] Sublimation temperature. − [b] Amount of condensed substance; condensation temperature 14°C. − [c] Amount of transported gas; nitrogen flow in each experiment 0.9 l h⁻¹. − [d] Vapor pressure at the indicated sublimation temperature, derived from the obtained amount of 2 by an interative method[30a,33].

Table 6. ESR coupling constants and signal width [G] of the 9-xanthyl radicals (7), the 7-benzanthryl radicals (9), and the 1-adamantyldiphenylmethyl radicals (4)

	7 MIRF[a]	TD[b]	9 MIRF[a]	TBO[c]	4 Reduction[d]
$a_{\alpha\text{-}H}$	12.65	12.64	8.55	8.55	-
$a_{b\text{-}H}$	-	-	-	-	0.50
$a_{\gamma\text{-}H}$	-	-	-	-	0.50
$a_{o\text{-}H}$	3.40	3.39	-	-	2.68
$a_{m\text{-}H}$	1.00	0.94	-	-	1.11
$a_{m'\text{-}H}$	1.00	0.94	-	-	-
$a_{p\text{-}H}$	3.98	4.07	-	-	2.77
$a_{x\text{-}H}$[e]	-	-	1.05	1.05	-
SW[f]	-	-	41.55	41.70	25.20

[a] Radical generation by hydrogen transfer reaction (for experimental conditions see text). − [b] Radicals generated by thermal dissociation (TD) of 9,9'-bixanthene at 182−187°C in napthalene[35]. − [c] Radicals generated by reaction of 7H-benzanthrene (8) with tert-butoxy radicals (TBO) formed from di-tert-butyl hyponitrite (for experimental conditions see text). − [d] Radicals generated by reaction of 1-adamantylchlorodiphenylmethane with copper powder (for experimental conditions see text). − [e] Smallest coupling constant in the spectrum of 9; for the complete set of a_H values measured by ENDOR see ref.[9c]. − [f] Signal width of the ESR spectrum.

cation 6.3 · 10⁵, frequency of the microwave 9.322 GHz, attenuation 15 dB. The measured coupling constants and the literature values are given in Table 6.

7-Benzanthryl Radicals (9): A solution of 2 (0.02 m) and 8 (0.1 m) in 1-(trimethylsilyloxy)-1-cyclohexene was heated under N₂ to 200°C. Spectrometer conditions: Magnetic strength in the middle of the spectrum 3330.0 G, modulation 0.08 G, amplification 1.25 · 10⁶, frequency of the microwave 9.324 GHz, attenuation 15 dB. The recorded spectrum is shown in Figure 1a. The smallest coupling constant, the α-coupling constant, and the width of the signal could be determined directly (see Table 6). For the generation of 9 in a different way a solution of di-tert-butyl hyponitrite (0.2 m) and 8 (0.1 m) was treated as described above. Spectrometer conditions: Magnetic strength in the middle of the spectrum 3326.0 G, modulation 0.125 G, amplification 1.60 · 10⁶, frequency of microwave 9.323 GHz, attenuation 15 dB. The spectrum is shown in Figure 1b. The obtained coupling constants and the signal width are listed in Table 6. By simulation using the complete set of a_H values[9c] the spectrum in Figure 1 was perfectly duplicated.

1-Adamantyldiphenylmethyl Radicals (4): 110 mg (0.33 mmol) of 1-adamantylchlorodiphenylmethane and 40 mg (0.63 mmol) of copper powder were heated in 0.7 ml of carefully degassed benzene in a sealed ESR tube at 110°C for 16 h. After cooling to 25°C, the ESR spectrum (see Figure 2a) was recorded. Spectrometer conditions: Magnetic strength in the middle of the spectrum 3327.5 G, modulation 0.032 G, amplification 2.00 · 10⁵, frequency of microwave 9.326 GHz, attenuation 15 dB. The spectrum was simulated with coupling constants for the aromatic protons which were similar to those of the tert-butyldiphenylmethyl radicals (Figure 2b). The coupling constants for the adamantyl protons were determined from the difference of the signal width and the sum of the aromatic coupling constants. The resulting coupling constants are compiled in Table 6.

[1] Part 5: M. Gerst, C. Rüchardt, *Tetrahedron Lett.* **1993**, in press.
[2] R. Schulze, H.-D. Beckhaus, C. Rüchardt, *Chem. Ber.* **1993**, *126*, 1031−1038, and references given there.
[3] H. Stetter, E. Rauscher, *Chem. Ber.* **1960**, *93*, 1161−1166.
[4] [4a] W. J. Middleton, *J. Org. Chem.* **1975**, *40*, 574−578. − [4b] A. L. Johnson, *J. Org. Chem.* **1982**, *47*, 5220−5222.
[5] J. W. Larson, T. B. McMahon, *J. Am. Chem. Soc.* **1983**, *105*, 2944−2950.
[6] [6a] C. Rüchardt, M. Gerst, M. Nölke, *Angew. Chem.* **1992**, *104*, 1516−1518; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1523−1525. − [6b] M. Gerst, C. Rüchardt, *Chem. Ber.* **1993**, *126*, 1039−1045. − [6c] C. Rüchardt, M. Gerst, J. Ebenhoch, H.-D. Beckhaus, E.

E. B. Campbell, R. Tellgmann, H. Schwarz, T. Weiske, S. Pitter, *Angew. Chem.* **1993**, *105*, 609−611; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 584−586. − [6d] M. Gerst, H.-D. Beckhaus, C. Rüchardt, E. E. B. Campbell, R. Tellgmann, *Tetrahedron Lett., im Druck.*

[7] J. A. K. Harmony in *Methods in Free Radical Chemistry* (Ed.: E. S. Huyser), vol. 5, Marcel Dekker, New York, **1974**, p. 101−176.

[8] V. R. Böhme, G. W. Jesse, *Chem. Phys. Lett.* **1969**, *3*, 3329−3334.

[9] [9a] G. D. Mendenhall, *Tetrahedron Lett.* **1983**, *24*, 451−452. − [9b] C. A. Ogle, S. W. Martin, M. P. Dziobak, M. W. Urban, G. D. Mendenhall, *J. Org. Chem.* **1983**, *48*, 3728−3733. − [9c] I. C. Lewis, L. S. Singer, *Magn. Reson. Chem.* **1985**, *23*, 698−704.

[10] [10a] A. R. Bassindale, A. J. Bowers, A. Hudson, R. A. Jackson, K. Schreiner, A. Berndt, *Tetrahedron Lett.* **1973**, *35*, 3185−3186. − [10b] K. Schreiner, A. Berndt, *Tetrahedron Lett.* **1973**, *41*, 4083−4086. − [10c] H. Sakurai, K. Mochida, M. Kira, *J. Organomet. Chem.* **1977**, *124*, 235−252. − [10d] J. Tino, E. Borsig, J. Pilar, *Collect. Czech. Chem. Commun.* **1969**, *34*, 66−71.

[11] A. G. Davies, A. G. Neville, *J. Chem. Soc., Perkin Trans. 2*, **1991**, 2021−2024.

[12] [12a] N. L. Allinger, *J. Am. Chem. Soc.* **1977**, *99*, 8127−8134. − [12b] A. Peyman, E. Hickl, H.-D. Beckhaus, *Chem. Ber.* **1987**, *120*, 713−725.

[13] J. P. Lorand, P. W. Wallace, *J. Am. Chem. Soc.* **1974**, *96*, 1402−1407.

[14] INDO calculations were performed by using the program QCPE 274.

[15] Values of k_2 determined at temperatures above 380°C, where the solvent was in a supercritical state, showed a poor correlation in the Eyring plot. Therefore, the activation parameters were determined at temperatures between 330 and 375°C.

[16] F. G. Bordwell, J. P. Cheng, G. Z. Ji, A. V. Satish, X. Zhang, *J. Am. Chem. Soc.* **1991**, *113*, 9790−9795.

[17] The deuteration level was 88% as determined by ¹H-NMR analysis.

[18] M. J. Bausch, R. Gostowski, G. Jirka, D. Seemarten, G. Winter, *J. Org. Chem.* **1990**, *55*, 5805−5806.

[19] [19a] ΔH_f^0(g) HF = −65.3 ± 0.2 kcal mol⁻¹: J. D. Cox, *J. Chem. Thermodyn.* **1976**, *8*, 603−605. − ΔH_f^0(g) DHA = 38.2 ± 1.1 kcal mol⁻¹ and ΔH_f^0(g) anthracene = 55.2 ± 0.5 kcal mol⁻¹: J. P. Pedley, R. D. Naylor, S. P. Kirby, *Thermochemical Data of*

Organic Compounds, 2nd Ed., Chapman and Hall, London, **1986**. − ΔH_f^0(g) **5** = 61.4 ± 1.5 kcal mol⁻¹: D. F. McMillen, D. M. Golden, *Ann. Rev. Phys. Chem.* **1982**, *33*, 493−532. − [19b] ΔH_f^0(g) of **3** = 20.2 kcal mol⁻¹ obtained from MM2[12] calculations. − [19c] H.-D. Beckhaus, B. Dogan, J. Schaetzer, S. Hellmann, C. Rüchardt, *Chem. Ber.* **1990**, *123*, 137−144. − [19d] J. A. Seetula, J. J. Russel, D. Gutman, *J. Am. Chem. Soc.* **1990**, *112*, 1347−1353.

[20] [20a] P. S. Engel, *Chem. Ber.* **1980**, *80*, 99−150. − [20b] M. Schmittel, C. Rüchardt, *J. Am. Chem. Soc.* **1987**, *109*, 2750−2759.

[21] [21a] C. Rüchardt, *Fortschr. Chem. Forsch.* **1966**, *6*, 251−300. − [21b] C. Rüchardt, V. Golzke, G. Range, *Chem. Ber.* **1981**, *114*, 2769−2785.

[22] J. Ebenhoch, Diplomarbeit, Universität Freiburg, **1993**.

[23] K. W. Egger, A. T. Cocks, *Helv. Chim. Acta* **1973**, *56*, 1516−1536.

[24] [24a] H.-D. Beckhaus, Dissertation, Universität Freiburg, **1975**. − [24b] H.-D. Beckhaus, J. Schoch, C. Rüchardt, *Chem. Ber.* **1976**, *109*, 1369−1383.

[25] H. C. House, L. J. Czuba, M. Gall, H. D. Olmstead, *J. Org. Chem.* **1969**, *34*, 2324−2336.

[26] B. R. Brown, A. M. S. White, *J. Chem. Soc.* **1957**, 3755−3757.

[27] Reinheitsmessung mit registrierender differentieller Kalorimetrie, *Analysentechnische Berichte* No. 45, Bodenseewerk, Perkin-Elmer & Co. GmbH, Überlingen, **1976**.

[28] R. J. Cvetanovic, D. L. Singleton, *Int. J. Chem. Kinet.* **1979**, *9*, 481−488.

[29] S. Sunner in *Combustion Calorimetry* (Ed.: S. Sunner, M. Mansson), Pergamon Press, Oxford, **1979**, p. 13.

[30] [30a] H.-D. Beckhaus, C. Rüchardt, M. Smisek, *Thermochim. Acta* **1984**, 149−159. − [30b] H.-D. Beckhaus, G. Kratt, K. Lay, J. Geiselmann, C. Rüchardt, B. Kitschke, H. J. Lindner, *Chem. Ber.* **1980**, *113*, 3441−3455.

[31] W. N. Hubbard, D. W. Scott, G. Waddington in *Experimental Thermochemistry* (Ed.: F. D. Rossini), Interscience Publishers, New York, **1956**, p. 75−127.

[32] J. D. Cox, G. Pilcher in *Thermochemistry of Organic Compounds*, Academic Press, London, **1970**.

[33] E. Hickl, H.-D. Beckhaus, Universität Freiburg, the program is available on request.

[34] *Chem-X*, Chemical Design Ltd., Oxford, England.

[35] M. D. Sevilla, G. Vincow, *J. Phys. Chem.* **1968**, *72*, 3635−3640.

[330/93]