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Rearrangement of the carbon skeleton in the intramolecular photoadduct of anthracene and benzene rings

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Abstract—The effectivity of optical switching between anthracene derivatives **3a**,**b** and their intramolecular photocycloadducts **4a**,**b** is impaired by traces of acid. The systematic treatment of **4a**,**b** with an increasing excess of formic acid revealed that—apart from the normal enolether cleavage **4a**,**b**→**6a**,**b**→**7a**,**b**—a cleavage with rearrangement of the carbon skeleton can occur: **5b**→**6b′**. The driving force is a stability enhancement of the involved carbenium ions **5b**→**5b′**. A further increased excess of formic acid leads finally to a competitive ether cleavage in the tetrahydrofuran ring **5b**→**8**. © 2003 Elsevier Science Ltd. All rights reserved.

1. Introduction

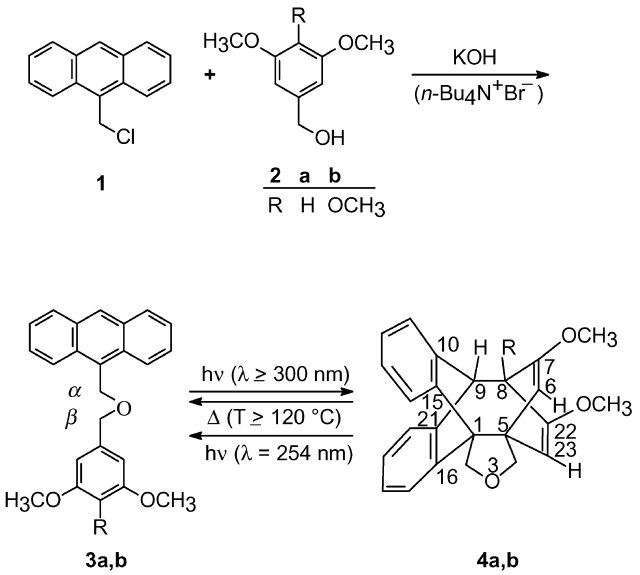
The anthracene chromophore attracts great attention in photochemistry because of its high capability of cycloaddition reactions.[1] Applications in materials science or molecular recognition seem to be particularly promising in the field of optical switching processes.[1–3]

Recently we prepared dendrimers with an anthracene core and dendrons of the Fréchet type and some model compounds for these light-harvesting systems.[4,5] Common to all these compounds is a benzene ring, which is linked by a CH_2–O–CH_2 chain to the 9-position of anthracene. A new type of [4π+4π] photocycloaddition was found, in which an electron-rich benzene ring adds in 1,4-position to the 9,10-position of the anthracene moiety.

The intramolecular variant[5] seems to be particularly suitable for optical switching processes since the photocycloaddition by irradiation into the anthracene chromophore as well as the reverse photoreaction with light of shorter wavelengths are quantitative processes. However, it turned out that the retrocycloaddition is impaired by the presence of traces of acid—on the surface of silica or in chloroform solution. Therefore we studied the influence of formic acid on two model systems that we now report.

2. Results and discussion

The reaction of 9-chloromethylanthracene (**1**) and di- or trimethoxybenzylalcohols (**2a**,**b**) leads under phase-transfer conditions in good yields to the anthracene derivatives **3a**,**b**. Irradiation (λ≥300 nm) of **3a**,**b** in a ~10^{-2} M solution in benzene furnishes the polycyclic compounds **4a**,**b** in quantitative yields (Scheme 1). The compounds **3a**,**b** exhibit the typical, 'finger-like' anthracene absorption with maxima at 333, 349, 367 and 387 nm (3.730≤log ε≤4.178). The cycloreversion can be quantitatively accomplished either by heating to 120°C or by irradiation with λ=254 nm.



Scheme 1. Preparation and reversible intramolecular cycloaddition of the anthracene derivatives **3a**,**b**.

Keywords: rearrangements; carbenium ions; ether cleavage; ketones.

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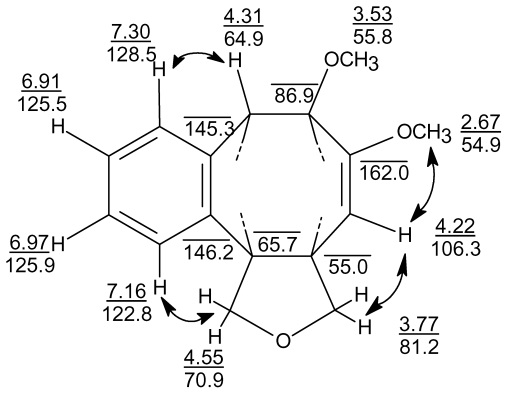
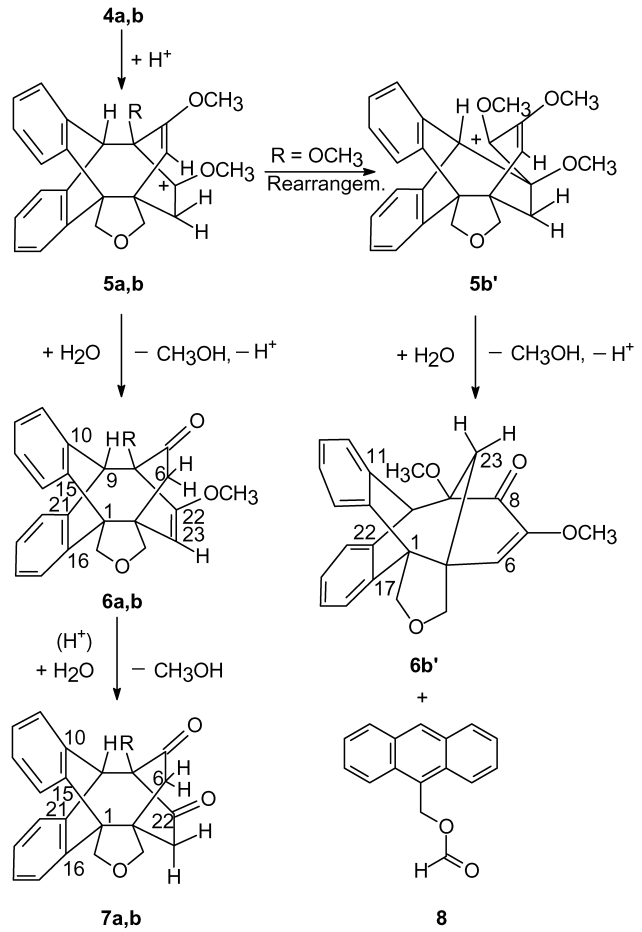


Figure 1. ^{1}H and ^{13}C NMR data of **4b** (C_s symmetry) in $CDCl_3$, related to TMS as internal standard. The arrows indicate the most important homonuclear NOEs.

The structure elucidation of **4a**,**b** is based on NMR and mass spectroscopic measurements. Figure 1 demonstrates the ^{1}H and ^{13}C chemical shifts of **4b**. The correlations with certain nuclei were obtained by nuclear Overhauser effect (NOE) measurements, homonuclear and heteronuclear shift correlations (HMQC and HMBC).

The treatment of **4a** with formic acid leads to a stepwise cleavage of the two enolether substructures. The transformation of **4a** to the monoketone **6a** and the diketone **7a** prevents a cycloreversion of the polycyclic system. The thermal activation barrier is probably too high because the retrocycloaddition would not restore the aromatic benzene rings; the reverse photoreaction fails presumably because of the formation of a first electronically excited singlet state S_1, which has a $n\pi^*$ character at the carbonyl groups (Scheme 2).

When **4b** is subjected to the same procedure, a surprising result is obtained. It turns out that the reaction route depends strongly on the molar ratio HCOOH–**4b** (Table 1). The formation of the monoketone **6b**, proved by ^{1}H NMR measurements, and of the isolated diketone **7b** is at room temperature a slow process, provided that a not much higher than fourfold excess of formic acid is used. When the ratio HCOOH–**4b** amounts to 10:1, the reaction rate of the enolether cleavage becomes high, but another product is generated. The normal $A-S_E2$ mechanism[6] for the enolether cleavage is almost completely suppressed, because the primary protonation generates a carbenium ion **5b**, which shows a rearrangement of the carbon skeleton. The driving



Scheme 2. Enolether cleavage of **4a**,**b** with formic acid.

force for the 1,2-C shift is rationalized by the formation of a more stable cation. The positive charge in **5b** and **5b′** is stabilized by the adjacent heteroatom O, but **5b′** represents additionally an allylic system.[7] The subsequent hydrolysis **5b′**→**6b′** yields an α,β-unsaturated monoketone **6b′**. Although **6b′** has still an enolether substructure, it is stable towards formic acid—even at 80°C. Diketone **7b** can be merely observed as a trace in the ^{1}H NMR spectrum of the raw product **6b′**. The latter measurement reveals another trace of a byproduct, namely the formate **8**. When the molar ratio HCOOH–**4b** is further changed to 13.7:1 and finally to 58.8:1, the amount of formed **6b′** is reduced and the percentage of **8** enhanced (Table 1). An extremely high excess of formic acid leads obviously to a competitive ether cleavage in the perhydrofuran ring (Scheme 2).[8]

Table 1. Product distribution in the acid-catalyzed cleavage of the bisenolether **4b** at room temperature

Entry	Molar ratio HCOOH–**4b**	Reaction time	Conversion (%)	Product distribution (%)		
				6b′	**7b**	**8**
1	4.1:1	10 d	100	–	100	–
2	8.2:1	12 h	60	20	80	–
3	10.3:1	1 h	100	100	Trace	Trace
4	13.7:1	2 h	100	95	–	5
5	58.8:1	1 h	100	74	–	26

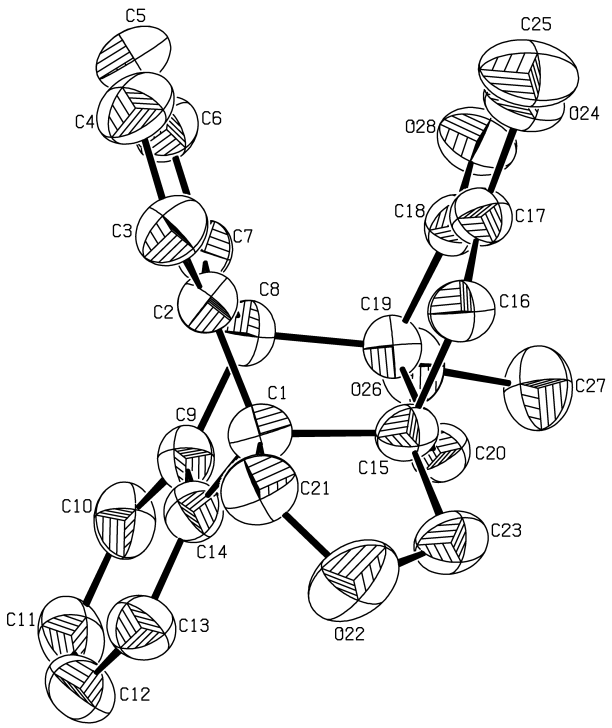


Figure 2. ORTEP plot of **6b′**. The displacement ellipsoids are shown at the 50% probability level. The numbering does not correspond to the nomenclature.

Apart from spectroscopic methods, the structure elucidation of **6b′** is based on an X-ray crystal structure analysis.[9] Figure 2 shows an ORTEP plot of **6b′**.

3. Conclusion

A quantitative optical switching between the anthracene derivatives **3a**,**b** and their polycyclic isomers **4a**,**b** requires an acid-free medium (or surface). In the presence of formic acid, **4a** and **4b** exhibit a normal enolether cleavage to the monoketones **6a**,**b** and the diketones **7a**,**b**. If however, the molar ratio of formic acid: **4b** is increased above a certain limit a competitive process **4b→6b′** can take place, which becomes then the major route. A 1,2-C-shift, based on the relative stability of the involved carbenium ions **5b** and **5b′**, is the characteristic step in the alternative ether cleavage. A further enhancement of the excess of HCOOH reduces finally the yield of **6b′**, because a new byproduct, namely the ester **8** is generated.

4. Experimental

4.1. General remarks

Melting points were measured on a Büchi melting point apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker AM 400 spectrometer. The mass spectra were obtained on a Finnigan MAT 95 spectrometer with the field desorption technique (FD) or with the electron impact method (EI) at 70 eV. The elemental analyses were determined in the Microanalytical Laboratory of the Chemistry Department of the University of Mainz.

4.2. General procedure for the preparation of the 9-(alkoxymethyl)antracenes 3a,b

A mixture of 9-chloromethylanthracene **1**[10] (454 mg, 2.0 mmol), 3,5-dimethoxybenzylalcohol **2a**[11] (370 mg, 2.2 mmol) or 3,4,5-trimethoxybenzylalcohol **2b**[12] (440 mg, 2.4 mmol), KOH (161 mg, 2.4 mmol), (*n*-Bu)$_4$NBr (90 mg, 0.28 mmol), 1 mL water and 20 mL chlorobenzene was stirred for 3–4 d at 65°C. The volatile parts were removed under reduced pressure (1 hPa) and the residue treated with 20 mL CH_2Cl_2 and 15 mL water. The separated water layer was three times extracted with 10 mL CH_2Cl_2 each. The combined organic phases were dried with Na_2SO_4 and the products purified by column chromatography (50×3 cm SiO_2, cyclohexane–ethylacetate 93:7).

4.2.1. 9-[(3,5-Dimethoxyphenyl)methoxymethyl]anthracene (3a). Yield 588 mg (82%), mp 100°C (ethanol–dichloromethane 1:1). ^{1}H NMR ($CDCl_3$): δ=3.76 (s, 6H, OCH_3), 4.65 (s, 2H, β-CH_2), 5.48 (s, 2H, α-CH_2), 6.43 (t, 1H, *p*-H, benzene), 6.57 (d, 2H, *o*-H, benzene), 7.48 (m, 4H, anthracene), 8.00 (m, 2H, anthracene), 8.32 (m, 2H, anthracene), 8.45 (s, 1H, 10-H, anthracene); ^{13}C NMR ($CDCl_3$): δ=55.3 (OCH_3), 64.0 (α-CH_2), 72.3 (β-CH_2), 100.1 (*p*-CH, benzene), 105.5 (*o*-CH, benzene), 124.3, 124.9, 126.1, 128.5, 129.0 (CH, anthracene), 128.7, 131.1, 131.5 (C_q, anthracene), 140.9 (*i*-C, benzene), 160.9 (*m*-C, benzene); EI MS: *m*/*z* (%)=358 (17) [M$^+$], 152 (100); Anal. calcd for $C_{24}H_{22}O_3$ (358.4): C, 80.42; H, 6.19. Found: C, 80.47; H, 6.21.

4.2.2. 9-[(3,4,5-Trimethoxyphenyl)methoxymethyl]anthracene (3b). Yield 488 mg (63%), viscous oil. ^{1}H NMR ($CDCl_3$): δ=3.79 (s, 6H, OCH_3), 3.85 (s, 3H, OCH_3), 4.62 (s, 2H, β-CH_2), 5.49 (s, 2H, α-CH_2), 6.58 (s, 2H, *o*-H, benzene), 7.48 (m, 4H, anthracene), 8.00 (m, 2H, anthracene), 8.32 (m, 2H, anthracene), 8.45 (s, 1H, 10-H, anthracene); ^{13}C NMR ($CDCl_3$): δ=56.0 (OCH_3), 60.8 (OCH_3), 63.9 (α-CH_2), 72.3 (β-CH_2), 104.7 (*o*-CH, benzene), 124.4, 125.0, 126.1, 128.6 (CH, anthracene), 128.5, 131.1, 131.5 (C_q, anthracene), 134.2 (*i*-C, benzene), 137.4 (*p*-C, benzene), 153.2 (*m*-C, benzene; FD MS: *m*/*z* (%)=389 (100) [M+H$^+$]. Anal. calcd for $C_{25}H_{24}O_4$ (388.5): C, 77.30; H, 6.23. Found: C, 77.20; H, 6.30.

4.3. Preparation of the photocycloadducts

4.3.1. 7,22-Dimethoxy-3-oxahexacyclo[7.6.6.2^{5,8}.0^{1,5}.0^{10,15}.0^{16,21}] tricosa-6,10,12,14,16,18,20,22-octaene (4a). A solution of 30 mg (8.4×10^{-2} mmol) of **3a** in 165 mL of benzene was purged with a slow stream of argon. After 30 min irradiation was started with a middle pressure mercury lamp (Hanovia 450 W) equipped with a Duran glass filter. The quantitative photocycloaddition was finished after 15 min, the solvent was removed and the product **4a** isolated as light yellow solid, which started to isomerize to **3a** at mp 98°C. ^{1}H NMR (C_6D_6): δ=2.82 (s, 6H, OCH_3), 3.42 (dd, ^3J=10.7 Hz, ^4J=2.4 Hz, 1H, 8-H), 3.90 (s, 2H, 4-H), 4.20 (d, ^3J=10.7 Hz, 1H, 9-H), 4.34 (d, ^3J=2.4 Hz, 2H, 6-H, 23-H), 4.70 (s, 2H,

2-H), 7.09 (m, 6H, aromat. H), 7.30 (m, 2H, aromat. H); ^{13}C NMR (C_6D_6): δ=51.3 (C-9), 53.3 (C-8), 54.8 (OCH_3), 56.9 (C-5), 65.7 (C-1), 71.2 (C-2), 81.1 (C-4), 105.8 (C-6, C-23), 122.8, 125.2, 125.8, 127.7 (aromat. CH), 145.0, 146.8 (aromat. C_q), 163.7 (C-7, C-22); FD MS: *m/z* (%)=359 (100) [M+H$^+$]. Anal. calcd for $C_{24}H_{22}O_3$ (358.4): C, 80.42; H, 6.19. Found: C, 80.44; H, 6.17.

4.3.2. 7,8,22-Trimethoxy-3-oxahexacyclo[7.6.6.2^{5,8}.0^{1,5}.0^{10,15}.0^{16,21}]tricosa-6,10,12,14,16,18,20,22-octaene (4b). 39 mg (0.10 mmol) **3b** yielded in the irradiation process, described above, 39 mg (100%) of **4b**, a yellow solid, which isomerizes to **3a** at mp 120°C. The ^{1}H and ^{13}C NMR data are shown in Figure 1. FD MS: *m/z* (%)=389 (100) [M+H$^+$]. Anal. calcd for $C_{25}H_{24}O_4$ (388.5). C, 77.30; H, 6.23. Found: C, 76.96; H, 6.42.

4.4. Enolether cleavage

4.4.1. (5*R**,8*R**)-22-Methoxy-3-oxahexacyclo[7.6.6.2^{5,8}.0^{1,5}.0^{10,15}.0^{16,21}]tricosa-10,12,14,16,18,20,22-heptaen-7-one (6a). To a solution of 20 mg (5.58×10^{-2} mmol) of **4a** in 3 mL toluene 0.02 mL (24.4 mg, 0.53 mmol) formic acid was added. After 25 min stirring at room temperature, the volatile parts were removed under reduced pressure. The raw product (19.2 mg, 100%), a yellowish solid was recrystallized from dichloromethane–cyclohexane (1:9). The thermally stable compound melted at 105°C. ^{1}H NMR ($CDCl_3$): δ=1.90/2.04 (AB, ^2J=−18.4 Hz, 2H, 6-H), 2.93 (s, 3H, OCH_3), 3.44 (dd, ^3J=11.7 Hz, ^4J=1.6 Hz, 1H, 8-H), 3.70/3.95 (AB, ^2J=−9.0 Hz, 2H, 4-H), 4.37 (s, 1H, 6-H), 4.38 (d, ^3J=11.7 Hz, 1H, 9-H), 4.68/4.88 (AB, ^2J=−10.6 Hz, 2H, 2-H); ^{13}C NMR ($CDCl_3$): δ=45.5 (C-6), 49.4 (C-9), 51.6, 60.4 (C-1, C-5), 54.6 (OCH_3), 60.6 (C-8), 72.0 (C-2), 81.0 (C-4), 105.9 (C-23), 122.9, 123.9, 125.9, 126.4, 127.0, 127.1, 127.5, 128.8 (aromat. CH), 140.2, 141.0, 141.6, 144.9 (aromat C_q), 158.8 (C-22), 209.7 (C-7); FD MS: *m/z* (%)=345 (100) [M+H$^+$]. Anal. calcd for $C_{23}H_{22}O_3$ (344.4): C, 80.21; H, 5.85. Found: C, 80.13; H, 5.90.

4.4.2. (5*R**,9*R**)-7,9-Dimethoxy-3-oxahexacyclo[8.6.6.1^{5,9}.0^{1,5}.0^{11,16}.0^{17,22}]tricosa-6,11,13,15,17,19,21-heptaen-8-one (6b′). To a solution of 39 mg (0.1 mmol of **4b** in 0.5 mL chloroform, 0.03 mL (36.6 mg, 0.795 mmol) of formic acid was added. After stirring at room temperature for 1 h, the volatile parts were removed under reduced pressure and the product **6b′** isolated in a quantitative yield. Colorless crystals, mp 189–190°C (dichloromethane–cyclohexane 1:9). ^{1}H NMR ($CDCl_3$): δ=1.32 (dd, ^2J=−12.6 Hz, $|^4J|$=1.9 Hz, 1H, *endo*-23-H), 2.45 (d, ^2J=−12.6 Hz, 1H, *exo*-23-H), 3.15 (s, 3H, OCH_3), 3.17 (s, 3H, OCH_3), 3.77/4.00 (AB, ^2J=−9.0 Hz, 2H, 4-H), 4.17 (s, 1H, 10-H), 4.74/4.88 (AB, ^2J=−9.9 Hz, 2-H), 5.35 (d, ^4J=1.9 Hz, 6-H), 6.94 (m, 1H, aromat. H), 7.05 (m, 2H, aromat. H), 7.19 (m, 4H, aromat. H), 7.52 (m, 1H, aromat. H); ^{13}C NMR ($CDCl_3$): δ=40.9 (C-23), 48.4, 59.7 (C-1, C-5), 51.9 (C-10), 55.0, 58.3 (OCH_3), 69.6, 80.5 (C-2, C-4), 78.7 (C-9), 121.6 (C-6), 122.0, 123.0, 126.9, 127.0, 127.0, 127.0, 127.8, 129.2 (aromat. CH), 138.9, 139.6, 141.7, 141.9 (aromat. C_q), 158.8 (C-7), 193.7 (C-8); FD MS: *m/z* (%)=375 (100) [M+H$^+$]. Anal. calcd for $C_{24}H_{22}O_4$ (374.2): C, 76.99; H, 5.92. Found: C, 76.93; H, 6.03.

4.4.3. 3-Oxahexacyclo[7.6.6.2^{5,8}.0^{1,5}.0^{10,15}.0^{16,21}]tricosa-10,12,14,16,18,20-hexaen-7,22-dione (7a). A solution of 20 mg (5.6×10^{-2} mmol) of **4a** in 0.5 mL of chloroform was treated with 0.05 mL (61.2 mg, 1.33 mmol) of formic acid. After 1 h stirring at room temperature, the volatile parts were removed under reduced pressure (1 hPa) and the raw product **7a** (18.4 mg, 100%) obtained as a colorless, thermally stable solid; mp 207°C (dichloromethane–cyclohexane 1:9). ^{1}H NMR ($CDCl_3$): δ=1.92/2.14 (AB, ^2J=−18.5 Hz, 4H, 6-H), 23-H), 3.80 (s, 2H, 4-H), 3.96 (d, ^3J=12.2 Hz, 1H, 8-H), 4.61 (d, ^3J=12.2 Hz, 1H, 9-H), 4.89 (s, 2H, 2-H), 7.28 (m, 6H, aromat. H), 7.50 (m, 2H, aromat. H); ^{13}C NMR ($CDCl_3$): δ=47.7 (C-6, C-23), 47.7 (C-9), 48.3, 56.7 (C-1, C-5), 72.5 (C-8), 73.5 (C-2), 81.2 (C-4), 124.5, 127.7, 127.9, 128.9 (aromat. CH), 138.4, 141.8 (aromat. C_q), 205.6 (C-7, C-22); FD MS: *m/z* (%)=331 (100) [M+H$^+$]. Anal. calcd for $C_{22}H_{18}O_3$ (330.4): C, 79.98; H, 5.49. Found: C, 79.96; H, 5.64.

4.4.4. 8-Methoxy-3-oxahexacyclo[7.6.6.2^{5,8}.0^{1,5}.0^{10,15}.0^{16,21}]tricosa-10,12,14,16,18,20-hexaen-7,22.dione (7b). To a solution of 25 mg (6.4×10^{-2} mmol) of **4b** in 3 mL toluene 0.01 mL (12.2 mg, 0.265 mmol) formic acid was added. After stirring for 10 d at room temperature, the volatile parts were removed under reduced pressure and the raw product **7b** (23.1 mg, 100%) obtained as a thermally stable, colorless solid; mp 241°C (dichloromethane–cyclohexane 1:9). ^{1}H NMR ($CDCl_3$): δ=2.03/2.13 (AB, ^2J=−18.8 Hz, 4H, 6-H, 23-H), 3.35 (s, 3H, OCH_3), 3.74 (s, 2H, 4-H), 4.35 (s, 1H, 9-H), 4.87 (s, 2H, 2-H), 7.28 (m, 6H, aromat. H), 7.35 (m, 2H, aromat. H); ^{13}C NMR ($CDCl_3$): δ=46.8, 56.0 (C-1, C-5), 48.6 (OCH_3), 56.5, 58.9 (C-6, C-9), 73.0 (C-2), 81.5 (C-4), 100.9 (C-9), 124.0, 127.8, 128.0, 129.3 (aromat. CH), 137.1, 141.9 (aromat. C_q), 203.4 (C-7, C-22); FD MS: *m/z* (%)=361 (100) [M+H$^+$]. Anal. calcd for $C_{23}H_{20}O_4$ (360.1): C, 76.65; H, 5.59. Found: C, 76.56; H, 5.54.

4.4.5. 9-Anthrylmethyl formate (8). A solution of 35 mg (9.0×10^{-2} mmol) of **4b** in 0.5 mL of chloroform was treated with 0.20 mL (244 mg, 5.30 mmol) formic acid. After 1 h stirring at room temperature, the volatile parts were removed under reduced pressure. The residue was separated by column chromatography (20×2 cm SiO_2, cyclohexane–ethyl acetate gradient 95:5 to 80: 20 to yield 5 mg (25%) of **8** as yellowish needles; mp 130°C. ^{1}H NMR ($CDCl_3$): δ=6.24 (s, 2H, CH_2), 7.53 (m, 4H, aromat. H), 8.03 (m, 2H, aromat. H), 8.19 (s, 1H, CHO), 8.32 (m, 2H, aromat. H), 8.52 (s, 1H, anthracene 10-H); ^{13}C NMR ($CDCl_3$): δ=58.2 (CH_2), 123.7, 125.2, 126.9, 129.2, 129.6 (aromat. CH), 128.0, 131.4, 134.1 (aromat. C_q), 161.1 (CHO); EI MS: *m/z* (%)=237 (61) [M+H$^+$], 192 (100); identification by comparison with an authentic sample.[13]

Acknowledgements

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6. See for example Smith, M. B.; March, J. *Advanced Organic Chemistry*. 5th ed., 2001; p 467.
7. Since **5e** does not show such a 1,2-C shift, both stabilizations of the cation seem to be a precondition for the rearrangement.
8. The remainder part of **4b** in the cleavage **4b→8** did not give a uniform compound, the ^{1}H NMR spectrum of the raw product contained for example six signals for methoxy groups bound to a benzene ring.
9. The crystallographic data of **6b′** have been deposited at Cambridge Crystallographic Data Centre as supplementary publication No. **6b′** CCDC 206152. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1 EZ, UK.
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