Photo-*Fries* Rearrangement of Carbazol-2-yl Sulfonates: Efficient Tool for the Introduction of Sulfonyl Groups into Polycyclic Aromatic Compounds

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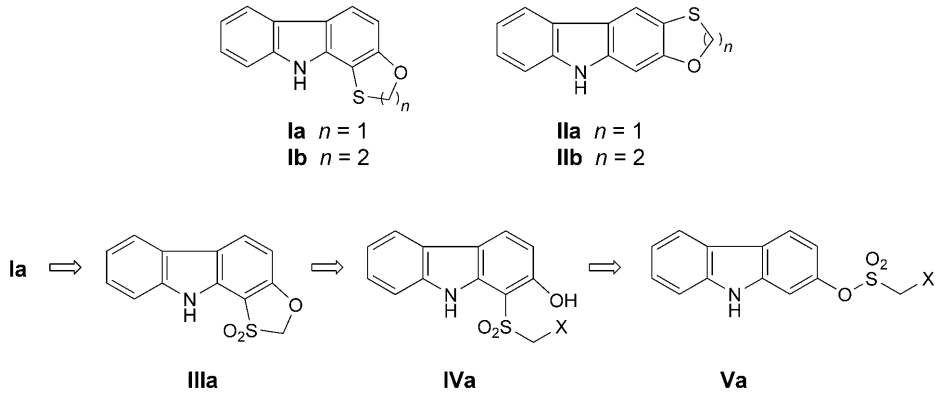
Systematic studies on the photo-*Fries* rearrangement of different 9*H*-carbazol-2-yl sulfonates **2** have shown that this type of conversion can be readily used for the preparative-scale introduction of alkyl- or arylsulfonyl groups into polycyclic aromatic compounds under very mild conditions. A series of new 1-sulfonyl- (**3**) or 3-sulfonyl-9*H*-carbazoles (**4**) were prepared in medium-to-good yields, and characterized by UV/VIS, ^{1}H-NMR, and ^{13}C-NMR spectroscopy, as well as by elemental analysis. Effects of irradiation wavelength, solvent polarity, presence or absence of O_2, and photosensitizers were studied in detail.

1. Introduction. – The introduction of S-atoms into single, polynuclear, or heteropolynuclear aromatic rings has received much attention during the last years [1]. Sulfurization of aromatic rings can be carried out with S_2Cl_2 or elemtal S in the presence of *Lewis* acids such as, *e.g.*, $AlCl_3$ [2]. This reaction has been used for ring closure. Also, $SOCl_2$ in the presence of $AlCl_3$ has been used as a reagent, but affords in a straightforward way diaryl sulfoxides. Unsymmetrical diaryl sulfides can be obtained by treatment of an aromatic compound with an arenesulfenyl chloride (ArSCl) in the presence of Fe powder [3]. However, unfortunately, the corresponding diphenyl disulfide is obtained in high yield as a major side product. Treatment of aromatic amines and phenols with dialkyl disulfides in the presence of *Lewis* acid catalysts such as CuI, $AlCl_3$, $TiCl_4$, or $ZrCl_4$ produces alkyl aryl sulfides, mostly as the *ortho* products [4]; also, elevated reaction temperatures (150–170°) are needed to accomplish the reaction. Finally, the *Herz* reaction can be used for the introduction of an S-atom into aromatic rings [5]. This reaction is carried out with an aniline and S_2Cl_2 in the presence of a base, generally NaOH. After acidic workup, 2-aminothiophenols are obtained. Nevertheless, this reaction is not suited as a general sulfurization method because good yields are obtained only when 4-chloroanilines are used as starting materials.

To circumvent these problems, we decided to explore the photo-*Fries* rearrangement of sulfonic ester derivatives as a suitable and general method for the introduction of S-atoms into aromatic moieties. In *Scheme 1*, a retrosynthetic, regioselective approach towards the new heterocyclic compounds **I** and **II** is shown, photo-*Fries* rearrangement being the key step. For example, to access **Ia**, synthon **IVa** can be prepared in one step by photo-*Fries* rearrangement of an adequate substrate such as **Va**. Cyclization of the resulting synthon **IVa** could be carried out with KOH in DMSO at room temperature to afford **IIIa** in good yield [6]. Finally, reduction with sulfur and

Scheme 1



heat [7], DIBAL in Et_2O [8], or $LiAlH_4$ in THF at low temperature [9] affords **Ia**. Likewise, the isomeric carbazole derivatives **IIa**,**b** can also be prepared from **Va** *via* this route.

The photo *Fries*-rearrangement has received considerable attention since its discovery in 1960 [10]. However, studies have been devoted mainly to elucidate the underlying reaction mechanism, rather than to explore the synthetic potential of the reaction [11]. Nevertheless, this photochemical reaction has been successfully used in the synthesis of natural products such as griseofulvin [12], daunomycine [13], and flavonoids [14].

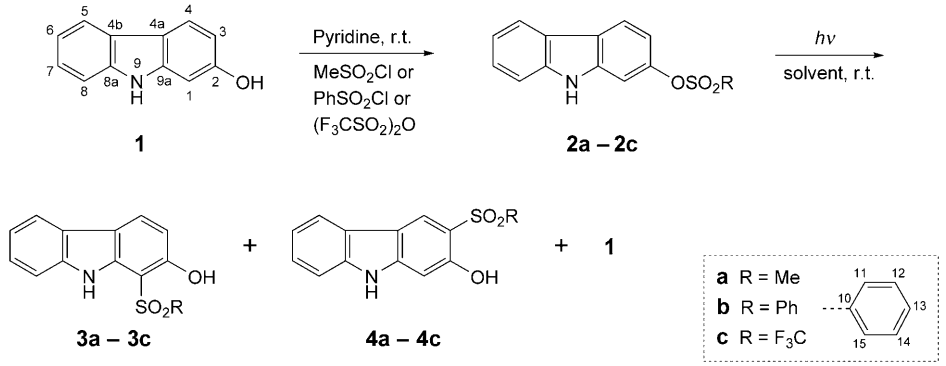
The photo-*Fries* rearrangement of aryl sulfonic esters has been scarcely investigated [15]; and, according to our knowledge, no attention has been paid to the photochemical behavior of aza-type heteroaromatic sulfonic esters such as carbazol-2-yl alkanesulfonates. The photo-*Fries* rearrangement is a mild and clean reaction, where no hazardous solvents or *Lewis* acids are needed. Also, the photoproducts are formed in good yields, with predictable regioselectivity.

In continuation of our research on photo-*Fries* reactions [16], we herein report a protocol for the efficient synthesis of various sulfonates of 9*H*-carbazol-2-ol (**1**), as well as their isolation and full characterization by means of physical and spectroscopic methods.

2. Results and Discussion. – 2.1. *Preparation and Characterization of Starting Materials.* Starting from 9*H*-carbazol-2-ol (**1**), compounds **2a**–**2c** required for photo-*Fries* rearrangement were prepared by acylation (*Scheme 2*). For the synthesis of **2a** and **2b**, we used methanesulfonyl chloride (MsCl) and benzenesulfonyl chloride, respectively, in the minimum volume of anhydrous pyridine at room temperature. Compounds **2a** and **2b** were obtained in excellent yields (> 95%) as colorless crystalline solids. For compound **2c**, trifluoromethanesulfonic anhydride, $(CF_3SO_2)_2O$, was used as acylating agent, which gave rise to a yield of 85%. In all these experiments, the molar ratio of acylating reagent to **1** was 1.1 to 1.0.

When the above acylations of **1** were performed in anhydrous benzene or CH_2Cl_2 in the presence of pyridine, the yields dropped substantially, and the reaction time was

Scheme 2



longer. This was particularly noteworthy for compound **2c**, where the chemical yield dropped from 85% (pyridine) to 45% (benzene/pyridine 3 : 1 (*v*/*v*)).

The sulfonates **2** were characterized by ^{1}H- and ^{13}C-NMR spectroscopy, including 2D-NMR experiments. Their ^{1}H-NMR spectra invariably showed the signals of H–C(4) and H–C(5) at δ(H) 7.90–8.20, which corresponds to a downfield shift (relative to those of **1**) due to inductive effects exerted by the sulfonyloxy groups attached to the carbazole moiety [17]. H–C(3) and H–C(1) of **2a**–**2c** resonated at δ(H) 7.04–7.46, and experienced a noticeable deshielding compared to the corresponding signals in **1**. The other H-atoms, H–C(6), H–C(7), and H–C(8), appeared at δ(H) 7.20–7.70, which is quite similar as in **1**.

In the ^{13}C-NMR spectra of compounds **2**, C(2) was observed at δ(C) 147.2–150.7, slightly upfield-shifted in comparison to C(2) of **1**. The signals for C(3) and C(1) were shifted downfield to δ(C) 99.9–114.7 due to inductive effects of the sulfonyloxy groups. Finally, while the signal for C(4) was shifted upfield by 4 ppm relative to that in **1**, the other resonances were hardly affected by acylation.

2.2. *Photoelectronic Properties of Starting Materials.* The UV-spectroscopic data of compounds **2a**–**c** are collected in *Table 1* for different organic media at 298 K. Generally, three bands centered at λ_{max} 245, 298, and 310 nm were observed. Comparison of previous spectroscopic data and theoretical calculations of carbazoles [18] with those of compound **2a** allowed us to assign the lowest-lying excited electronic states of the bands located at 298 and 310 nm as ^1L_a ($S_2 \rightarrow S_0$) and ^1L_b ($S_1 \rightarrow S_0$) electronic transitions, respectively. On changing the solvent polarity, a bathochromic shift of 2–6 nm was observed, which suggests that the nature of the lowest singlet-excited state most likely corresponds to a $\pi \rightarrow \pi^*$ transition [19].

Excitation at 310 nm induced a fluorescence emission at 320–370 nm. The high-energy edge of the emission spectrum overlapped well with the 0–0 absorption band. The nearly negligible amount of *Stokes*' shift reflects a high structural similarity between the ground and the excited states. Similar spectroscopic features were also observed for the analogs **2b** and **2c**.

The phosphorescence emission spectra of compounds **2a**–**2c** were recorded in a frozen matrix of i-PrOH/Et_2O 1 : 1 at 77 K. Excitation at 310 nm induced phosphorescence at 400–600 nm, with λ_{max} values at 407, 410, and 407 nm, respectively, for **2a**, **2b**, and **2c**.

Table 1. *Spectroscopic Data of* **2a**–**c** *in Different Media*. Unless stated otherwise, the experiments were performed at ambient temperature under Ar atmosphere.

Compound	Solvent	λ_{max} [nm]			E_T [kcal/mol]
		Absorption	Fluorescence	Phosphorescence	
2a	Cyclohexane	334	355		
	MeCN	334	351		
	MeOH	336	351		
	Solid matrix[a])			407	69.8
2b	Cyclohexane	336	355		
	MeCN	335	355		
	MeOH	336	357		
	Solid matrix			410	69.5
2c	Benzene	335	346		
	MeCN	334	346		
	MeOH	335	355		
	Solid matrix			409	69.7

[a]) In i-PrOH/Et_2O 1:1 frozen at 77 K.

The energy of the lowest triplet-excited state (E_T) of these compounds was readily estimated at 69.5–69.8 kcal/mol (*Table 1*).

2.3. *Photo*-Fries *Rearrangement in Solution*. Irradiation of a 6 mM solution of 9*H*-carbazol-2-yl methanesulfonate (**2a**) in benzene, cyclohexane, MeCN, or MeOH at 313 nm under Ar atmosphere at room temperature afforded the *ortho*-migrated products **3a** and **4a**, together with **1** and methanesulfonic acid (*Scheme 2*). The reaction was followed both spectrophotometrically and by HPLC analysis. After irradiation, the products were separated by column chromatography (SiO_2), and were identified and characterized (see *Exper. Part*). Irradiation of compounds **2b** and **2c** under similar conditions yielded the corresponding *ortho*-rearrangement products **3b** and **4b**, and **3c** and **4c**, respectively, along with **1**. The yields of these transformations are collected in *Table 2* for different solvents.

The pairs of *ortho*-rearranged products, *i.e.*, **3a**/**4a**, **3b**/**4b**, and **3c**/**4c**, were all obtained in a molar ratio of *ca.* 2:1. As shown in *Table 2*, the C(1)-rearrangement products **3a**–**3c** were the main products formed in yields of *ca.* 60%. The C(3)-rearrangement products **4a**–**4c** were side products (*ca.* 25% yield). In all experiments, compound **1** was observed, resulting from acyl cleavage rather than rearrangement. These results are similar to those obtained previously for the irradiation of 2-acetyloxy- and 2-(benzoyloxy)carbazoles [16c].

To rationalize the observed regioselectivity in the above transformations, we performed semi-empirical and *ab initio* optimizations of the 2-hydroxy-9*H*-carbazole radical. The charge density at C(1) was found to be slightly higher than at C(3). Additionally, the carbazole NH might assist the acyl rearrangement through H-bonding, a process that, for geometric reasons, is possible only for the rearrangement to C(1), not to C(3). Therefore, both factors, a slightly higher charge density at C(1) and the possibility of a H-bridge assisting in the rearrangement may account for the observed regioselectivity in favor of the 1-substituted product.

Table 2. *Product Distribution upon Irradiation of* **2a**–**c** *in Different Media*. Conditions: substrates **2**, 6 mM; excitation at 313 nm; $T = 298$ K; Ar atmosphere; conversion > 90%.

Substrate	Solvent	Yield [%][a])		
		3	**4**	**1**
2a	MeCN	61.5	27.0	9.5
	MeOH	65.7	23.3	11.0
	Benzene	60.0	24.5	10.5
	Cyclohexane	58.1	23.5	11.4
2b	MeCN	57.6	26.2	10.5
	MeOH	67.3	22.5	10.3
	Benzene	54.5	22.6	9.9
2c	MeCN	64.8	24.3	10.8
	MeOH	68.4	23.8	10.8
	Benzene	55.6	21.6	16.8

[a]) Determined by HPLC analysis.

The rearranged products **3** and **4** are described and characterized herein for the first time. They can be synthesized under very mild conditions at room temperature by means of the photo-*Fries* rearrangement in moderate-to-good yields. The present experimental conditions are advantageous over the thermal *Fries* rearrangement, where higher temperatures (80–120°) and *Lewis* acid catalysts such as $AlCl_3$ or $FeCl_3$ are required [20].

2.4. *NMR Properties of Rearrangement Products.* The ^{1}H-NMR spectra of the 1-substituted products **3** invariably showed the signal of H–C(4) at δ(H) *ca.* 8 due to the known deshielding at the *peri*-positions in the carbazole moiety. The signals of H–C(3) appeared at δ(H) 6.84–6.94. The signals of H–C(5), H–C(6), H–C(7), and H–C(8) appeared in the range δ(H) 7.20–8.10, which is quite similar to the corresponding chemical shifts in the starting materials. The ^{13}C-NMR spectra of **3a**–**3c** showed the signals for C(2) and C(1) at δ(C) *ca.* 163 and 105, respectively. The other C-atoms showed chemical shifts in the same range as those of the respective starting materials.

In the ^{1}H-NMR spectra of the 3-substituted carbazoles **4a**–**4c**, H–C(4) was observed as δ(H) 8.4 (*s*) due to the deshielding effect at the *peri*-positions. The signal of H–C(1) appeared at δ(H) *ca.* 6.85 (*s*). H–C(5), H–C(6), H–C(7), and H–C(8) resonated in the range δ(H) 7.20–8.10. The ^{13}C-NMR spectra of these compounds invariably showed the signals for C(2) and C(3) at δ(C) *ca.* 164 and 119, respectively. The other C-atoms showed chemical shifts in the same range as those of the respective starting materials.

2.5. *Photophysical Considerations.* To characterize the multiplicity of the reactive excited states of compounds **2**, we carried out additional experiments. Irradiation of the starting materials in MeOH in the presence of air or O_2 did not show any change in the distribution of the rearrangement products, although both rate of conversion and yield were slightly lower under these conditions. This minor effect suggests that O_2 does not quench the reactive excited state. Also, no significant difference in the product ratio was observed when compounds **2a**, **2b**, or **2c** were irradiated in MeOH or benzene at 254 and 313 nm (*Table 3*). These results suggests that the lowest excited

Table 3. *Product Distribution upon Irradiation of* **2a**–**c** *in MeOH* vs. *Benzene.* Conditions: substrates **2**, 6 mM; excitation at 254 nm; $T = 298$ K; Ar atmosphere; conversion > 90%.

Substrate	Solvent	Yield [%][a])		
		3	**4**	**1**
2a	MeOH	63.5	24.3	11.0
	Benzene	61.0	20.5	10.5
2b	MeOH	66.0	21.2	10.5
	Benzene	55.2	21.6	10.1
2c	MeOH	67.4	21.3	9.5
	Benzene	55.6	21.6	16.8

[a]) Determined by HPLC analysis.

state is the chemically reactive state involved in the photorearrangement, which, probably, is a singlet state.

Next, we carried out *photosensitized* reactions of 6 mM solutions of **2a**–**2c** in MeCN under Ar atmosphere by exciting at 366 nm in the presence of 10 mM xanthone as a triplet-energy donor [21]. The results are shown in *Table 4*. In solution, xanthone was the only substrate capable of absorbing light, and of populating the triplet-excited state of the carbazole substrates through a triplet-energy-transfer process. This process is exergonic because the E_T value of xanthone (74 kcal/mol) is higher than those of compounds **2** (69.5 kcal/mol; see above). However, the photo-*Fries* rearrangement of **2** did not take place upon photosensitization with xanthone. Therefore, we concluded that the triplet-excited state of these substrates did not provide the observed rearrangement products.

Next, 50 mM solutions of **2** in MeCN were irradiated separately at 310 nm under Ar gas in the presence of 1 mM 'tetramethyl-1,2-diazetine dioxide' (TMDD), a triplet-energy quencher (E_T 54 kcal/mol) [21], under Ar gas. In these experiments, only the substrates **2** absorbed light at 310 nm. Now, in the presence of TMDD, a regular photo-*Fries* rearrangement was observed (*Table 4*). Thus, the photoreactive lowest-excited state of these compounds is the singlet-excited state. These results clearly show *i*) that compounds **2** populate efficiently the S_1 state by direct absorption of light; *ii*) that the photoreactive excited state affording the *ortho*-rearrangement products is the S_1 state ($\pi \rightarrow \pi^*$); and *iii*) that the photosensitized formation of the triplet-excited state does not yield any stable photoproduct; indeed, this triplet-excited state should be deactivated efficiently at room temperature through radiationless pathways.

It is interesting to point out that the photoreactive excited states of compounds **2a**–**2c** are similar to those of excited *N*-acetyl- and *N*-benzoyl-9*H*-carbazole [16a,b], as well as of the corresponding 2-substituted congeners [16c]. This means that the population of the singlet-excited state, which is the photoreactive excited state, is independent of the position where the Ac or SO_2 groups are attached to the carbazole moiety.

Finally, the quantum yields (ϕ) for the photo-*Fries* rearrangement of **2a**–**2c** were determined in different organic media using 'potassium ferrioxalate' (= potassium tris(oxalato)ferrate(III)) as actinometer [22–24]. These measurements were conducted

Table 4. *Photosensitization and Quenching of Substrates* **2** *in MeCN*. Conditions: substrate concentration, 6.0 mM; $T = 298$ K; Ar atmosphere; conversion > 90%.

Substrate	Additive	λ_{exc} [nm]	Yield [%][a])		
			3	**4**	**1**
2a	None	313	61.5	27.0	9.5
	TMDD[b])	313	61.3	27.4	10.5
	Xanthone[c])	366	no reaction		
2b	None	313	57.6	26.2	10.5
	TMDD	313	56.2	25.8	9.5
	Xanthone	366	no reaction		
2c	None	313	64.8	24.3	10.8
	TMDD	313	62.1	22.5	9.8
	Xanthone	366	no reaction		

[a]) Determined by HPLC analysis. [b]) 'Tetramethyl-1,2-diazetine dioxide', used as triplet quencher. [c]) Used as triplet photosensitizer.

Table 5. *Quantum Yields for the Photo*-Fries *Conversion of Compounds* **2**. The experiments were conducted both in the absence and presence of O_2.

Substrate	Solvent	Quantum yield[a])	
		Anaerobic[b])	Aerobic
2a	MeCN	0.13	0.12
	MeOH	0.09	0.09
	Benzene	0.13	0.13
2b	MeCN	0.22	0.21
	MeOH	0.18	0.19
	Benzene	0.17	0.17
2c	MeCN	0.18	0.18
	MeOH	0.21	0.21
	Benzene	0.12	0.12

[a]) Determined at low conversion (< 10%) of starting material at λ_{exc} 313 nm. For details, see *Exper. Part*. [b]) Ar Atmosphere.

both under aerobic and anaerobic conditions. The conversions of the starting materials were monitored by HPLC analysis, and the quantum yields determined are listed in *Table 5*. As can be seen, the ϕ values did not depend significantly on the presence or absence of O_2. This means that dissolved O_2 did not quench efficiently the singlet-excited states of the substrates, which is in agreement with the results presented in *Tables 2* and *3*. However, the ϕ values of **2a**–**2c** were moderately dependent on solvent polarity, which suggests that the reaction intermediates are, to some extent, stabilized preferentially in polar solvents.

3. Conclusions. – We have shown that *ortho*-rearranged products of type **3** and **4** can be obtained in good yield and under very mild conditions from the corresponding 9*H*-carbazol-2-yl sulfonates **2** through photo-*Fries* rearrangement on preparative scale, and

with significant regioselectivity. The rearrangement involves an 'in-cage' 1,3-type migration of the RO_2SO or ArO_2SO moiety, 9*H*-carbazol-2-ol (**1**) being formed as an 'out-of-cage' side product. From a synthetic point of view, photo-*Fries* rearrangement provides interesting *ortho*-rearranged products as potential synthons for the preparation of 1,3-thioxolane and 1,4-thioxolane rings fused to the carbazole moiety. This synthetic approach, thus, represents a convenient tool for the introduction of sulfur functional groups in polycyclic aromatic compounds. We have also shown that, mechanistically, the lowest singlet-excited state of the carbazole substrates is the photoreactive excited state yielding the *ortho*-rearranged products.

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Experimental Part

General. Xanthone, 'tetramethyldiazetine dioxide' (TMDD), benzenesulfonyl chloride, methanesulfonyl anhydride, and trifluoromethanesulfonyl anhydride were purchased from *Aldrich*, and were used without further purification. Compound **1** was purchased from *Aldrich*, and purified by column chromatography (CC). Spectrograde solvents were obtained from *J. T. Baker*, and used as received. Column chromatography (CC): *Merck* silica gel *60* (0.040–0.063 mm). TLC: *Merck* silica gel *60* F_{254} on Al sheets (0.2 mm thickness). Melting points (m.p.): *Fisher-Jones* apparatus; uncorrected. ^{1}H- and ^{13}C-NMR Spectra: *Bruker AC-200* spectrometer; chemical shifts δ in ppm rel. to Me_4Si, J in Hz. UV/VIS Spectra: *Shimadzu UV-1203* spectrophotometer; in 1-cm stoppered quartz cells, at 298 K; λ_{max} in nm. Fluorescence and phosphorescence spectra: *Hitachi F-500* spectrofluorometer; at r.t. in 1-cm stoppered quartz cells, and in the 90° mode. Measurement at 77 K were made in transparent matrices prepared by freezing i-PrOH/Et_2O 1:1 with liquid N_2 in a 2-mm cylindrical cell.

General Procedure for the Synthesis of Compounds **2**. To a soln. of **1** (1 g, 5.46 mmol) in anh. pyridine (10 ml), a soln. of the appropriate alkane- or benzenesulfonyl chloride (6.05 mmol) in pyridine (5 ml) was added dropwise over 15 min, while the mixture was gently stirred at 0°. The mixture was then stirred for 3 h at r.t. (TLC and HPLC control). After completion of the reaction, the mixture was poured into H_2O (50 ml). The resulting brownish solid was separated, and extracted with $CHCl_3$ (2×20 ml). The combined org. layers were washed with 10% aq. HCl, dried ($MgSO_4$), and concentrated *in vacuo*. The solid residue was purified by filtration over a short pad of SiO_2 (hexane/AcOEt 7:3) to afford the corresponding product.

9H-*Carbazol-2-yl Methanesulfonate* (**2a**). Yield: 1.40 g (98.2%). Colorless solid. M.p. 96°. ^{1}H-NMR (200 MHz, (D_6)DMSO): 11.50 (*s*, NH); 8.20 (*d*, *J*=8.0, H–C(5)); 8.15 (*d*, *J*=8.4, H–C(4)); 7.53 (*d*, *J*=8.0, H–C(6)); 7.46 (*d*, *J*=1.8, H–C(1)); 7.40 (*d*, *J*=7.6, H–C(7)); 7.22 (*d*, *J*=7.6, H–C(8)); 7.14 (*dd*, *J*=1.8, 8.4, H–C(3)); 3.38 (*s*, Me). ^{13}C-NMR (50 MHz, (D_6)DMSO): 150.7 (C(2)); 144.0 (C(9a)); 143.3 (C(8a)); 129.4 (C(7)); 124.6 (C(4)); 123.8 (C(5)); 122.6 (C(6)); 122.3 (C(4b)); 121.8 (C(4a)); 116.3 (C(8)); 114.7 (C(3)); 99.9 (C(1)); 40.7 (Me). Anal. calc. for $C_{13}H_{11}NO_3S$ (261.30): C 59.76, H 4.24, N 5.36, S 12.27; found: C 59.72, H 4.23, N 5.45, S 12.25.

9H-*Carbazol-2-yl Benzenesulfonate* (**2b**). Yield: 1.68 g (95.2%). Colorless solid. M.p. 124°. ^{1}H-NMR (200 MHz, (D_6)DMSO): 8.14 (*s*, NH); 8.01 (*d*, *J*=7.7, H–C(5)); 7.89 (*d*, *J*=8.4, H–C(4)); 7.86 (*d*, *J*=8.0, 2 arom. H); 7.76 (*t*, *J*=7.3, H–C(6)); 7.51 (*t*, *J*=7.3, H–C(7)); 7.46–7.39 (*m*, 3 arom. H); 7.27 (*d*, *J*=7.3, H–C(8)); 7.18 (*d*, *J*=1.8, H–C(1)); 7.64 (*dd*, *J*=1.8, 8.4, H–C(3)). ^{13}C-NMR (50 MHz, (D_6)DMSO): 147.2 (C(2)); 140.5 (C(9a)); 139.9 (C(8a)); 135.2 (C(10)); 134.2 (C(13)); 129.1 (C(12,14)); 128.5 (C(11, 15)); 126.0 (C(7)); 122.3 (C(4a)); 122.1 (C(4b)); 120.6 (C(4)); 120.1 (C(5)); 119.5 (C(6)); 113.0 (C(8)); 110.9 (C(3)); 104.9 (C(1)). Anal. calc. for $C_{18}H_{13}NO_3S$ (323.37): C 66.86, H 4.05, N 4.33, S 9.92; found: C 66.75, H 4.00, N 4.35, S 9.96.

9H-Carbazol-2-yl Trifluoromethanesulfonate (**2c**). Yield: 1.46 g (84.8%). Colorless solid. M.p. 92°. ^{1}H-NMR (200 MHz, (D_6)DMSO): 11.50 (*s*, NH); 8.20 (*d*, *J* = 8.0, H–C(5)); 8.15 (*d*, *J* = 8.4, H–C(4)); 7.53 (*d*, *J* = 8.0, H–C(6)); 7.46 (*d*, *J* = 1.8, H–C(1)); 7.40 (*d*, *J* = 7.6, H–C(7)); 7.22 (*d*, *J* = 7.6, H–C(8)); 7.14 (*dd*, *J* = 1.8, 8.4, H–C(3)). ^{13}C-NMR (50 MHz, (D_6)DMSO): 147.6 (C(2)); 140.4 (C(9a)); 139.3 (C(8a)); 126.8 (C(7)); 120.4 (C(4)); 121.3 (C(5)); 120.4 (C(6)); 123.3 (C(4b)); 122.3 (C(4a)); 115.8 (F_3C); 112.5 (C(8)); 111.0 (C(3)); 103.8 (C(1)). Anal. calc. for $C_{13}H_8F_3NO_3S$ (315.27): C 49.53, H 2.56, F 18.08, N 4.44, S 10.17; found: C 49.73, H 2.58, F 18.02, N 4.43, S 10.13.

General Procedure for the Preparative-Scale Photo-Fries *Rearrangement of* **2**. Through a soln. of the substrate (1.5 mmol) in the appropriate solvent (250 ml) in a quartz immersion well was bubbled Ar gas for 20 min. The soln. was irradiated at 313 nm under gentle stirring with a medium-pressure Hg lamp (*Hereaus TQ150*) for 2–3 h. Alternatively, irradiation at 254 nm was carried out with a low-pressure Hg lamp (*Hanau TNQ 15*), and the progress of the reaction was monitored by TLC (SiO_2; hexane/AcOEt 4:1) and HPLC (*RP-18*; MeCN/H_2O 7:3, 1.0 ml/min; detection at 310 nm). The photolysis soln. was concentrated *in vacuo*, and the resulting yellowish oily residue was purified by CC (SiO_2; hexane/AcOEt) to afford the corresponding photoproducts.

1-(Methylsulfonyl)-9H-carbazol-2-ol (**3a**). Yield: 254 mg (64.8%). Colorless solid. M.p. 170–171°. ^{1}H-NMR (200 MHz, $CDCl_3$): 11.99 (*s*, NH); 8.55 (*s*, OH); 8.10 (*d*, *J* = 8.8, H–C(4)); 8.01 (*dd*, *J* = 1.9, 8.8, H–C(5)); 7.40–7.20 (*m*, H–C(6,7,8)); 6.84 (*d*, *J* = 8.8, H–C(3)); 2.91 (*s*, Me). ^{13}C-NMR (50 MHz, $CDCl_3$)): 163.0 (C(2)); 140.1 (C(9a)); 139.8 (C(8a)); 124.9 (C(7)); 124.6 (C(4)); 123.2 (C(4b)); 120.9 (C(5)); 119.1 (C(6)); 113.3 (C(4a)); 110.9 (C(8)); 103.8 (C(3)); 103.1 (C(1)); 39.8 (Me). Anal. calc. for $C_{13}H_{11}NO_3S$ (261.30): C 59.76, H 4.24, N 5.36, S 12.27; found: C 59.71, H 4.23, N 5.42, S 12.29.

3-(Methylsulfonyl)-9H-carbazol-2-ol (**4a**). Yield: 91.2 mg (23.3%). Colorless solid. M.p. 216–218°. ^{1}H-NMR (200 MHz, $CDCl_3$): 12.7 (*s*, NH); 8.41 (*s*, H–C(4)); 8.15 (br. *s*, OH); 7.99 (*d*, *J* = 7.8, H–C(5)); 7.4–7.2 (*m*, H–C(6,7,8)); 6.86 (*s*, H–C(1)); 2.77 (*s*, Me). ^{13}C-NMR (200 MHz, $CDCl_3$)[1]): 162.3 (C(2)); 145.4 (C(9a)); 140.3 (C(8a)); 125.9 (C(7)); 123.6 (C(4b)); 120.7 (C(5)); 120.6 (C(4)); 119.6 (C(6)); 119.1 (C(3)); 116.8 (C(4a)); 110.7 (C(8)); 97.3 (C(1)); 41.9 (Me). Anal. calc. for $C_{13}H_{11}NO_3S$ (261.30): C 59.76, H 4.24, N 5.36, S 12.27; found: C 59.73, H 4.22, N 5.40, S 12.31.

1-(Phenylsulfonyl)-9H-carbazol-2-ol (**3b**). Yield: 362 mg (74.6%). Colorless solid. M.p. 205°. ^{1}H-NMR (200 MHz, $CDCl_3$): 12.20 (*s*, NH); 8.16 (*d*, *J* = 8.4, H–C(4)); 7.92 (*dd*, *J* = 1.5, 7.0, H–C(5)); 7.73 (*dd*, *J* = 7.5, 2 arom. H); 7.67–7.58 (*m*, 3 arom. H); 7.37 (br. *s*, OH); 7.30 (*dd*, *J* = 1.5, 7.3, H–C(6)); 7.24 (*dt*, *J* = 1.8, 7.3, H–C(7)); 7.08 (*dt*, *J* = 1.8, 8.04, H–C(8)); 6.94 (*d*, *J* = 8.4, H–C(3)). ^{13}C-NMR (50 MHz, $CDCl_3$): 163.3 (C(2)); 140.0 (C(9a)); 139.1 (C(8a)); 138.1 (C(10)); 132.4 (C(13)); 129.5 (C(11,15)); 129.2 (C(7)); 127.6 (C(12,14)); 124.8 (C(4)); 122.7 (C(4b)); 120.5 (C(5)); 119.0 (C(6)); 116.9 (C(4a)); 110.5 (C(3,8)); 105.3 (C(1)). Anal. calc. for $C_{18}H_{13}NO_3S$ (323.37): C 66.86, H 4.05, N 4.33, S 9.92; found: C 66.81, H 4.03, N 4.36, S 9.95.

3-(Phenylsulfonyl)-9H-carbazol-2-ol (**4b**). Yield: 109.0 mg (22.5%). Colorless solid. M.p. 218–220°. ^{1}H-NMR (200 MHz, $CDCl_3$): 12.7 (*s*, NH); 8.41 (*s*, H–C(4)); 8.01 (*dd*, *J* = 1.5, 7.0, H–C(5)); 8.15 (*dd*, *J* = 8, H–C(11,15)); 7.45–7.55 (*m*, H–C(12,13,14)); 7.54 (*dd*, *J* = 1.5, 7.3, H–C(6)); 7.27 (*dt*, *J* = 1.5, 7.3, H–C(7)); 7.15 (*dt*, *J* = 1.5, 8.0, H–C(8)); 6.90 (*s*, H–C(1)). ^{13}C-NMR (50 MHz, $CDCl_3$): 172.5 (C(2)); 145.2 (C(9a)); 140.1 (C(8a)); 138.1 (C(10)); 132.4 (C(13)); 129.5 (C(11,15)); 128.4 (C(7)); 127.6 (C(12,14)); 125.9 (C(4)); 122.2 (C(4b)); 120.7 (C(5)); 119.8 (C(6)); 117.2 (C(3)); 115.3 (C(4a)); 110.8 (C(8)); 97.6 (C(1)). Anal. calc. for $C_{18}H_{13}NO_3S$ (323.37): C 66.86, H 4.05, N 4.33, S 9.92; found: C 66.92, H 4.06, N 4.31, S 9.90.

1-[(Trifluoromethyl)sulfonyl]-9H-carbazol-2-ol (**3c**). Yield: 321 mg (67.9%). Colorless solid. M.p. 134–136°. ^{1}H-NMR (200 MHz, $CDCl_3$): 11.99 (*s*, NH); 8.55 (*s*, OH); 8.10 (*d*, *J* = 8.8, H–C(4)); 8.01 (*d*, *J* = 1.9, 8.8, H–C(5)); 7.40–7.20 (*m*, H–C(6,7,8)); 6.84 (*d*, *J* = 8.8, H–C(3)). ^{13}C-NMR (50 MHz, $CDCl_3$): 163.0 (C(2)); 140.1 (C(9a)); 139.8 (C(8a)); 124.9 (C(7)); 124.6 (C(4)); 123.2 (C(4b)); 120.9 (C(5)); 119.1 (C(6)); 115.2 (F_3C); 113.3 (C(4a)); 110.9 (C(8)); 103.8 (C(3)); 103.1 (C(1)). Anal. calc. for $C_{13}H_8F_3NO_3S$ (315.27): C 49.53, H 2.56, F 18.08, N 4.44, S 10.17; found: C 49.65, H 2.57, F 18.04; N 4.42, S 10.14.

3-[(Trifluoromethyl)sulfonyl]-9H-carbazol-2-ol (**4c**). Yield: 110 mg (23.3%). Colorless solid. M.p. 196–198°. ^{1}H-NMR (200 MHz, $CDCl_3$): 12.7 (*s*, NH); 8.41 (*s*, H–C(4)); 8.15 (br. *s*, OH); 7.99 (*d*, *J* = 7.8, H–C(5)); 7.4–7.2 (*m*, H–C(6,7,8)); 6.86 (*s*, H–C(1)). ^{13}C-NMR (200 MHz, $CDCl_3$): 162.3

(C(2)); 145.4 (C(9a)); 140.3 (C(8a)); 125.9 (C(7)); 123.6 (C(4b)); 120.7 (C(5)); 120.6 (C(4)); 119.6 (C(6)); 119.1 (C(3)); 116.8 (C(4a)); 115.9 (F_3C); 110.7 (C(8)); 97.3 (C(1)). Anal. calc. for $C_{13}H_8F_3NO_3S$ (315.27): C 49.53, H 2.56, F 18.08, N 4.44, S 10.17; found: C 49.62, H 2.58, F 18.03, N 4.41, S 10.18.

Determination of Chemical Quantum Yields for Photo-Fries *Rearrangements.* Solns. of the appropriate substrate **2** (0.55 mmol) were prepared in different organic solvents (10 ml). An aliquot (2 ml) of each soln. was placed in a spectrophotometric quartz cell, through which Ar gas was bubbled during 20 min. Similarly, a 6 mM soln. of 'potassium ferrioxalate' ($K_3Fe(C_2O_4)_3 \cdot 3\ H_2O$) was prepared, an aliquot (2 ml) was placed in a spectrophotometric quartz cell, and Ar gas was bubbled through the soln. for 20 min. The cells were then placed in an optical bench, and irradiated simultaneously with a medium-pressure Hg lamp (*Hereaus TQ150*), whose radiation was collimated with a *Schott* quartz lens, and filtered with an interference *Schott* filter (5-nm path band) to give a nearly parallel beam at 313 nm. The chemical quantum yields ϕ were then determined with 'potassium ferrioxalate' as an actinometer according to the procedure described in [23]. The conversions of **2a**–**2c** were monitored by HPLC, and were lower than 10%.

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