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Stereochemistry of the Addition of Bromine to Acenaphthylene Derivatives: Substituent and Solvent Effects

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Summary. Addition of bromine to acenaphthylene and 5-bromoacenaphthylene in aprotic solvents of different polarity is not stereospecific: both *trans* and *cis* isomers of the corresponding 1,2-dibromides are formed. In general, the relative proportion of *syn* addition increases with decreasing solvent polarity; the highest percentage of *cis* products is observed in 1,4-dioxane. The stereochemistry of bromine addition to nine additional 3-, 5-, and 5,6-substituted acenaphthylenes in dioxane is reported. A number of new *cis*-1,2-dibromoacenaphthenes have been isolated for the first time.

Keywords. Acenaphthene derivatives; Electrophilic addition; Stereoselectivity; Solvent effects.

Stereochemie der Addition von Brom an Derivate des Acenaphthylens: Einflüsse von Substituenten und Lösungsmitteln

Zusammenfassung. Die Addition von Brom an Acenaphthylen und 5-Bromacenaphthylen erfolgt in aprotischen Lösungsmitteln unterschiedlicher Polarität unspezifisch: sowohl *cis*- als auch *trans*-Produkte werden gebildet. Allgemein steigt der Anteil der *syn*-Addition mit steigender Polarität des Lösungsmittels, wobei der stärkste Effekt bei 1,4-Dioxan beobachtet wird. Die Stereochemie der Bromaddition an neun weitere 3-, 5- und 5,6-Acenaphthylenderivate wird beschrieben; einige *cis*-1,2-Dibromacenaphthenderivate wurden erstmals erhalten.

Introduction

It is well known that the electrophilic addition of bromine to aliphatic alkenes proceeds stereospecifically as an *anti* process due to the intermediate formation of the well documented cyclic bromonium ion **1** [1]. The addition of bromine to aryl substituted double bonds, however, proceeds *via* an open carbenium ion (**2**, [2–10]) and therefore lacks stereospecifity. In these cases, both *syn* and *anti* addition are possible at the planar center.

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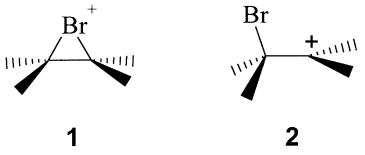


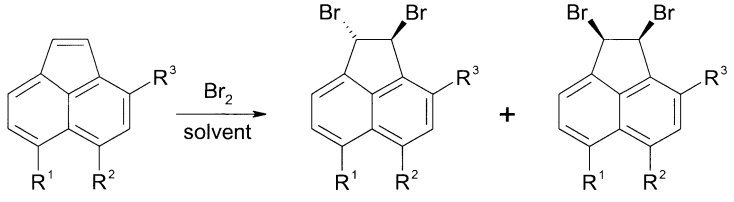
1 **2**

Formula Scheme 1

The equilibrium **1**⇌**2** for aryl substituted olefins strongly depends on the electron donating ability of the aromatic ring (substituent effect) [8–10] and on the reaction medium [11]. It has been shown that the stereoselectivity increases with the electron deficiency of the substituent [9] and with decreasing solvent polarity [2–5]. This effect was ascribed to a stabilization of the cyclic intermediate by acceptors and non-polar solvents [5,6]. For the bromination of stilbenes in protic solvents the mY_{Br} relationships, the chemoselectivity, and the high dependence of the stereochemistry on the solvent and the substituents have been discussed in terms of a mechanistic scheme, in which preassociation, free-ion, and ion-pair pathways compete [8]. It has also been suggested that bromonium bridging is substituent, but not solvent dependent [8].

Acenaphthylene is structurally closely related to *cis*-stilbene, but the conformationally rigid 5-membered ring does not allow any internal rotation in cationic intermediates of type **2**. Hence, changes in the resulting *cis*/*trans* ratios due to the intermediate isomerization can be excluded, but substituent and solvent effects should be similar. As has been shown earlier, acenaphthylene halogenation proceeds opposite to the stilbene tendency: the amount of *syn* addition increases in *less polar* solvents [6]. Based on the dependence of kinetics and stereochemistry of acenaphthylene bromination in chlorinated solvents on concentration and solvent polarity, a rationalization involving tight and solvent-separated ion pair intermediates has been proposed [7].

The present work is devoted to the establishment of reaction conditions in favour of *cis*-1,2-dibromoacenaphthenes. Only 3-halogeno- and 5-bromoderivatives of *cis*-1,2-dibromoacenaphthene have been described before [12, 13]. To find the suitable solvent for the preferred formation of *cis*-dibromides, we have undertaken a study of the stereochemistry of bromination of acenaphthylene (**3a**)



3a-k **4a-k** **5a-k**

	a	b	c	d	e	f	g	h	i	j	k
R^1	H	H	H	H	H	H	H	H	Br	Cl	NO_2
R^2	H	Br	Cl	F	Bz	NO_2	H	H	Br	Cl	NO_2
R^3	H	H	H	H	H	H	NO_2	Cl	H	H	H

Formula Scheme 2

and 5-bromoacenaphthylene (**3b**) in aprotic solvents of widely varying polarity. Having found a suitable solvent, the stereochemistry of the bromination of some 3-,5-, and 5,6-substituted acenaphthylenes (**3c–k**) was investigated.

Results and Discussion

All bromination reactions were carried out at 0–6°C in aprotic solvents of various polarities ($1.9 < \varepsilon < 38.5$) and specific nucleophilic solvation ability. The *cis*/*trans* ratios of 1,2-dibromoacenaphthenes (**4** and **5**) were determined by integration of the signals of the methyne protons (H1, H2) in the ^{1}H NMR spectra of **4** and **5** which differ by *ca.* 0.05 ppm (see Table 4) and by a UV method making use of the significant rate differences of the dehydrobromination of *cis*- and *trans*-1,2-dibromides **4** and **5** with *i*PrOK in *i*PrOH ($k_{cis}/k_{trans} > 10^3$). As shown in Table 1, the average difference of the two methods is close to $\pm 2\%$.

The results of this investigation show that the electrophilic bromination of **3a** and **3b** is nonstereospecific in all solvents applied and that the bromine substituent of **3b** causes only small changes of *cis*/*trans* ratio in comparison with **3a** (Table 1). By variation of the reaction medium *trans* addition ranges from 40 to 90% (Table 1). It has already been shown [**7**] that the bromination products **4a** and **5a** can be formed in reactions of different kinetic order. If the stereoisomeric dibromides are formed under kinetic control, which seems reasonable, the *cis*/*trans* ratio can be directly used for the evaluation of k_{cis}/k_{trans} [4]. However, all attempts to find a linear correlation between ln(*cis*/*trans*) and solvent parameters such as ε, $(\varepsilon-1)/(2\varepsilon+1)$, E_T, nucleophilicity *B*, or *DN* [14] were unsuccessful. For solvents of similar solvation properties (*e.g. THF*, Et_2O, dioxane), however, there is a good correlation of ln(*cis*/*trans*) values and the *Kirkwood* function (Fig. 1) [15]

Table 1. Percentage of *syn* addition of molecular bromine to acenaphthylenes **3a**,**b** in different solvents[1]

Solvent	ε[2]	**5a**(%)		**5b**(%)	
		NMR[3]	UV	NMR[3]	UV
Hexane	1.89	26	28; 50[4]	31	30
1,4-Dioxane	2.21	56	61	54	56
Carbon tetrachloride	2.23	29	32; 34[4]	30	31
Benzene	2.27	50	43	44	42
Toluene	2.38	43	38	40	39
Diethyl ether	4.20	23	20[4]	20	18
Chloroform	4.81	32	38[4]	35	38
Chlorobenzene	5.62	39	–	33	31
Tetrahydrofuran	7.58	11	8[4]	5	–
1,2-Dichloroethane	10.37	26	–	20	29
Acetonitrile[5]	35.94	10	8	11	13
Nitromethane[5]	35.94	13	14	5	–

[1] 0.1 g of **3a** and **3b** in 5 ml of solvent, $T = 0$–6°C; [2] see Ref. [14]; [3] values used for correlation analysis; [4] from Ref. [6]; [5] 0.1 g in 15 ml

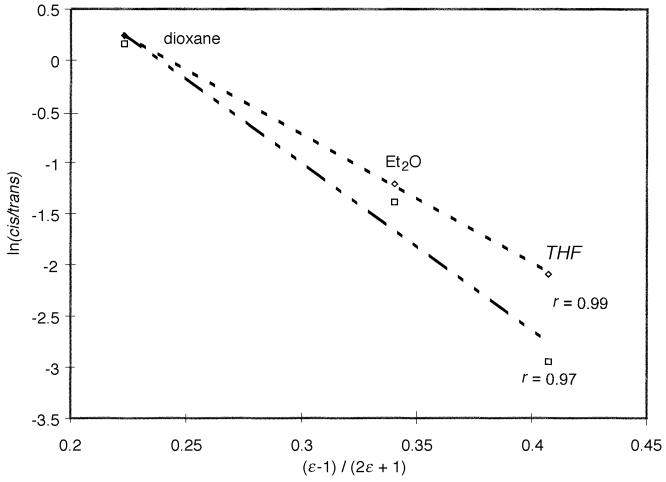


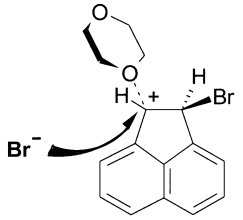
Fig. 1. Plot of ln(*cis*/*trans*) *vs. Kirkwood* function for the bromine addition to acenaphthylene **3a** (- - - -) and 5-bromoacenaphthylene **3b** (– —)

The obtained data support the participation of tight and solvent-separated ion pairs during the process [6, 7]. Non-specific solvents of low polarity such as hexane or carbon tetrachloride do not assist the ionization of ion pairs. Under these conditions, translocation of the counteranion should be sufficiently slow and, as a result, the *trans* stereoselectivity of addition will decrease. Additionally, the low bromine concentration at an approximately 1:1 ratio of Br_2 and alkene does not favour the formation of the L-shaped polybromide species Br_5^- or Br_7^- which could transfer a Br^- ion directly to the *anti* position. [7]

Increasing the solvent polarity should favour ion pair separation and increase the lifetime of solvated ions and, thereby, enable a more facile translocation of the counter anion. Indeed, in the most polar solvents the amount of *trans* adducts increases; however, noticeable quantities of *cis* dibromides **5a**,**b** are still observed in all solvents used. Therefore, for the bromination of acenaphthylenes **3a**,**b** we can exclude the cyclic bromonium ion and explain the results of addition in terms of the open carbenium ion **2** as a more or less separated ion. Furthermore, semiempirical PM3 calculations [17] of the possible bromination intermediates of **3a** have shown that the open 2-bromoacenaphthyl cation is more stable than its cyclic isomer, whereas the cyclic bromonium intermediate is preferred in the bromination of ethene [18].

In 1,4-dioxane, the bromination of the acenaphthylenes **3a**,**b** gave the highest amount of *syn* product. Remarkably, the *syn*/*anti* ratio is well above unity, and it should be mentioned that the bromination of acenaphthylene **3a**, under comparable conditions, never led to more than 50% of *cis* product in any solvent previously used for this reaction. [6, 19–21]

A possible rationalization of the dioxane effect could be the participation of the well-documented dioxane bromine complex. However, bromination of **3a** with the dioxane bromine complex in benzene solution gave the same result as with bromine only. Thus, the *bulk* dioxane must be effective in the determination of the stereochemistry. Furthermore, tetrahydrofuran and diethyl ether also give similar



6

Formula Scheme 3

1:1-complexes with bromine in solutions with comparable stabilities (ΔH_f (kcal/mol): 2.0 (dioxane), 3.5 (*THF*), 5.5 (ether) [22]), but the *cis*-preference is shown only by dioxane.

A reasonable explanation for the excess of the *cis* dibromides is a specific participation of 1,4-dioxane in the solvation of the bromocarbenium ion like in **6**. A tighter solvation of **6** by the oxygen atom of the dioxane molecule from the backside would block that site and direct the bromide ion in a fashion to afford the *cis* dibromide. A similar intermediate has been suggested in the interpretation of the remarkably high proportion of *syn* addition of bromine to *Z*-1-phenylpropene in dioxane [4]. The fact that the same *threo*/*erythro* product mixture was formed from *E*-1-phenylpropene seems to prove that the same type of dioxane solvated bromocation is involved in all cases.

The observed dioxane effect on the stereochemistry led us to study a set of acenaphthylene derivatives with various substituents in dioxane. It was interesting to study the influence of substituents on the stereochemistry of bromination in this solvent. Another aspect was the preparation of new *cis*-1,2-dibromoderivatives of substituted acenaphthenes (**5c–k**). It should be mentioned that *cis*-1,2-dibromoacenaphthene has been prepared only recently [6], whereas the *trans* isomer has been known for more than a century [19].

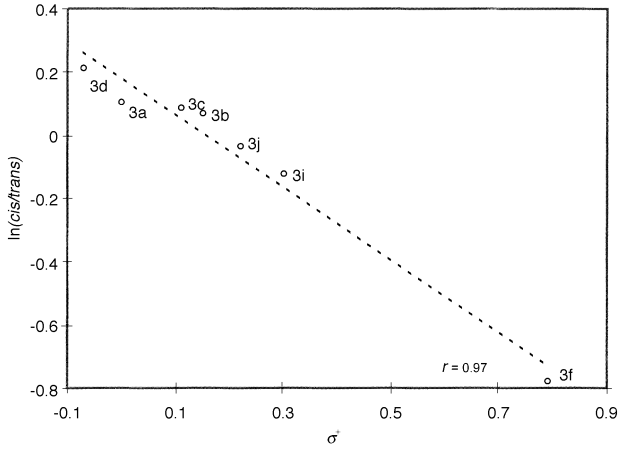


Fig. 2. Plot of ln(*cis*/*trans*) *vs.* σ^+ constants for the bromination of 5- and 5,6-substituted acenaphthylenes

Table 2. *Cis/trans* ratio of products (**5/4**) of the bromination of acenaphthylenes **3a–k** in 1,4-dioxane

	3a	**3b**	**3c**	**3d**	**3e**	**3f**	**3g**	**3h**	**3i**	**3j**	**3k**
5/4[1]	56/44	54/46	55/45	62/38	56/44	14/86	14/86	44/56	43/57	48/52	–[2]

[1] By NMR analysis; [2] high *trans* selectivity, ≤2% *cis*

In summary, the bromination of acenaphthylenes **3a–k** in dioxane leads to an appreciably high proportion of *cis*-dibromides (Table 2). From the corresponding acenaphthylenes in dioxane, the *cis* 1,2-dibromides **5c–g,i,j** were isolated for the first time. (Table 3). As a rule, the *cis*-isomers have higher melting points and smaller R_f values (silical gel, hexane) than their *trans* isomers and melt with decomposition. This observation is in accordance with the properties of diastereomeric *cis* and *trans* 1,2-dichlorides of halogeno substituted acenaphthenes [23].

A satisfactory *Hammett* plot with $r = 0.97$ and a slope of -1.17 was obtained using σ^+ constants corresponding to the cationic character of the transition state (Fig. 2). As is commonly accepted [10], the rate determining step of the addition process is the solvent assisted ionization of the initial π-complex. With increasing electron withdrawing character of the substituent in the naphthalene system, the rate of formation of a cationic intermediate will decrease. The bromonium ion – open or bridged – will bear a higher charge by which ion separation and *anti* attack will be favoured. In effect, *cis*-1,2-dibromo-5,6-dinitroacenaphthene **5k** could not be detected at all in the bromination of **3k**.

As for the 1,2-dibromides **4a,b** and **5a,b**, the signals of methyne protons (H1, H2) for the *cis* species are shifted downfield by *ca.* 0.05 ppm compared with the *trans* isomers (Table 4). Also, for *cis*-isomers with a non-symmetrical substitution pattern in the aromatic ring (**5b–h**), the coupling constant J_{12} for H1 and H2 ranges from 5 to 7 Hz, whereas for *trans*-1,2-dibromides this value is very small (0 to 1 Hz, Table 4) in accordance with the *Karplus* equation [24] for torsional angles H1–C1–C2–H2 for *cis* and *trans* isomers of 15° and 110°, respectively.

Experimental

General

Acenaphthylene **3a** (Fluka, 98%) was recrystallized from ethanol, acenaphthylenes **3b–d,f–k** were prepared according to literature procedures [25–29]. ^{1}H NMR: Bruker WM-250 or Bruker ARX 400, $CDCl_3$ as a solvent, *TMS* as internal standard; UV/Vis: Specord UV-Vis, SF-26 (Russia); Elemental analysis: Analytical Laboratory of the University of Regensburg; Melting points (uncorrected): Büchi 510 apparatus. Solvents were purified by recommended procedures [30] prior to use. Reaction mixtures resulting from the bromination of acenaphthylene and its derivatives were protected from light.

5-Benzoylacenaphthylene (**3e**)

A mixture of 1.16 g($4.5 \cdot 10^{-3}$ mol) of 5-benzoylacenaphthene and 1.45 g ($6.4 \cdot 10^{-3}$ mol) 2,3-dichloro-5,6-dicyanobenzoquinone-1,4 (Merck, 98%) in benzene (20 ml) was refluxed for 14 h.

Chromatographic separation (silica gel, 1.5×20 cm, benzene) and recrystallization from ethanol afforded 0.49 g of **3e** (42%).

Bright yellow crystals; m.p.: 72–73°C; UV/Vis (*i*PrOH): λ_{max} (l gε) = 332.4 (4.09), 352.1 (3.77) nm, ^{1}H NMR ($CDCl_3$): δ = 7.06 (d, J = 5.3 Hz, 1H, H1), 7.18 (d, J = 5.3 Hz, 1H, H2), 7.45–8.01 (m, 10 H, aromatic protons); $C_{19}H_{12}O$ (256.3); calcd.: C 89.04, H 4.72; found: C 88.95, H 4.60.

trans-1,2-Dibromo-5-benzoylacenaphthene (**4e**)

To a solution of 5-benzoylacenaphthene (10 g, 0.039 mol) in carbon tetrachloride (150 ml), a solution of bromine (4 ml, 12.48 g, 0.078 mol) in 15 ml of carbon tetrachloride was added dropwise under irradiation by 2 external 200 W lamps, stirring, and reflux during 30 min. Then the mixture was refluxed with stirring for 30 min. The solution was washed with warm aqueous sodium carbonate, water, and dried ($CaCl_2$). The solvent was evaporated, and the red residue was recrystallized three times from hexane (1:200) giving 1.2 g (7.5%) of **4e**.

Yellowish crystals; m.p.: 88–90°C; $C_{19}H_{12}Br_2O$ (416.1); calcd.: C 54.84, H 2.91; found: C 54.66, H 3.15.

Table 3. Conditions of preparation and characterization of **5a–g,i,j**

Reaction conditions					Characterization		Elemental analysis				
	3 (mmol/ml)	excess Br_2	reaction time	workup[1]	m.p. (°C) appearance	yield (%)	formula	calcd.		found	
								C	H	C	H
5a	0.094	1.1	30	A	121–122 (acetone) [6] colourless plates or needles	44					
5b	0.077	1.1	30	A	124.5–125.5 (ethanol) [13] colourless needles	36					
5c	0.127	1.1	30	A	110.5–111.5 (ethanol) long colourless needles	27	$C_{12}H_7Br_2Cl$	41.60	2.04	40.63	2.39
5d	0.196	1.1	30	B	121–122 colourless needles	5	$C_{12}H_7Br_2F$	43.68	2.14	43.75	2.30
5e	0.078	1.1	30	B	yellow oil	7	$C_{19}H_{12}Br_2O$	54.84	2.91	54.88	3.10
5f	0.085	1.5	120	C	135–136 pale yellow crystals	10	$C_{12}H_7Br_2NO_2$	40.39	1.98	40.30	2.17
5g	0.085	1.5	120	C	138–139 yellow crystals	10	$C_{12}H_7Br_2NO_2$	40.39	1.98	40.45	2.15
5i	0.141	1.1	30	A	154.5–156 (ethanol) pale yellow needles	29	$C_{12}H_6Br_2Cl_2$	37.84	1.59	37.90	1.85
5j	0.169	1.1	30	A	149.5–151.5 (ethanol) reddish plates	28	$C_{12}H_6Br_4$	30.68	1.29	30.44	1.62

[1] A: The residue is washed with ether (2×5 ml) and crystallized from ethanol or acetone; B: the residue is dissolved in 2 ml of CH_2Cl_2 and passed through a prepacked column size B (310×25), LiChroprep Si60 (40–63 μm), eluent: hexane/CH_2Cl_2 (3:1), second fraction; C: the residue is separated by preparative TLC (silica gel, hexane), isomer with the lower R_f value

Table 4. [1]H NMR data of *cis*- and *trans*-1,2-dibromoacenaphthene derivatives (δ, ppm)

	H_1	H_2	H_3	H_4	H_5	H_6	H_7	H_8
4a	6.00 s		7.81 q	7.61 q	7.59 q		7.61 q	7.81 d
			$J_{34} = J_{78} = 6.2$ Hz		$J_{67} = J_{45} = 7$ Hz		$J_{68} = J_{35} = 2.7$ Hz	
5a	6.03 s		7.75 q	7.57 q	7.55 q		7.57 q	7.75 d
			$J_{34} = J_{78} = 5.4$ Hz		$J_{67} = J_{45} = 7$ Hz		$J_{68} = J_{35} = 2$ Hz	
4b	5.93 d	5.98 d	7.46 d	7.86 d	–	8.01 d	7.73 q	7.65 d
	$J_{12} = 0.8$ Hz		$J_{34} = 7.5$ Hz			$J_{67} = 8.2$ Hz	$J_{78} = 7$ Hz	
5b	5.98 d	6.03 d	7.42 q	7.82 d	–	7.95 d	7.70 q	7.63 d
	$J_{12} = 6.25$ Hz		$J_{34} = 7.5$ Hz			$J_{67} = 8.2$ Hz	$J_{78} = 7.1$ Hz	
4c	5.94 s	5.99 s	7.51 d	7.67 d	–	8.06 d	7.72 q	7.65 d
			$J_{34} = 7.5$ Hz			$J_{67} = 7.9$ Hz	$J_{78} = 7.1$ Hz	
5c	6.01 d	6.05 d	7.49 d	7.64 d	–	8.01 d	7.71 q	7.63 d
	$J_{12} = 6.3$ Hz		$J_{34} = 7.5$ Hz			$J_{67} = 8.4$ Hz	$J_{78} = 7.1$ Hz	
4d	5.95 s	6.00 s	7.52 oct	7.24 q	–	7.95 d	7.64 t	7.68 d
			$J_{34} = 7.8$ Hz, $J_{H3F} = 3.2$ Hz, $J_{H4F} = 10.9$ Hz			$J_{67} = 6.7$ Hz	$J_{78} = 7.1$ Hz	
5d	6.01 d	6.05 d	7.49 oct	7.25 q	–	7.91 d	7.64 t	7.60 d
	$J_{12} = 6.3$ Hz		$J_{34} = 7.5$ Hz, $J_{H3F} = 4.0$ Hz, $J_{H4F} = 11.3$ Hz			$J_{67} = 7.5$ Hz	$J_{78} = 7.1$ Hz	
4e	6.02 s	6.05 s	7.65 d	7.84 d	8.24 m (1 H)[1]	7.71 d	7.69 q	7.63 d
			$J_{34} = 7.2$ Hz		7.51 t (2 H)	$J_{67} = 7.5$ Hz	$J_{78} = 7.3$ Hz	
					7.9 d (2 H)			
5e	6.05 d	6.10 d	7.62 d	7.81 d	8.17 m (1 H)[1]	7.70 d	7.66 q	7.60 d
	$J_{12} = 6.3$ Hz		$J_{34} = 7.5$ Hz		7.85 d (2 H)	$J_{67} = 7.2$ Hz	$J_{78} = 7.0$ Hz	
					7.49 t (2 H)			
4f	5.94 d	6.00 d	7.67 d	8.62 d	–	8.75 d	7.91 q	7.76 d
	$J_{12} = 1$ Hz		$J_{34} = 7.8$ Hz			$J_{67} = 8.7$ Hz	$J_{78} = 7.1$ Hz	
5f	6.02 d	6.10 d	7.66 d	8.61 d	–	8.71 d	7.89 q	7.75 d
	$J_{12} = 6.35$ Hz		$J_{34} = 7.8$ Hz			$J_{67} = 8.6$ Hz	$J_{78} = 7.2$ Hz	
4g	6.06 d	6.51 d	–	8.35 d	8.00 d	7.95 d	7.84 q	7.79 d
	$J_{12} = 0.9$ Hz			$J_{45} = 9.0$ Hz		$J_{67} = 7.7$ Hz	$J_{78} = 7.0$ Hz	
5g	6.00 d	6.60 d	–	8.31 d	7.95 d	7.89 d	7.83 q	7.73 d
	$J_{12} = 5.7$ Hz			$J_{45} = 9.0$ Hz		$J_{67} = 8.2$ Hz	$J_{78} = 6.9$ Hz	
4h	5.96 t	6.00 q	–	7.78 d	7.51 d	7.80 d	7.60 t	7.64 d
	$J_{12} = 0.5$ Hz			$J_{45} = 8.7$ Hz		$J_{67} = 7.4$ Hz	$J_{78} = 7.1$ Hz	
5h	5.95 d	6.03 d	–	7.74 d	7.49 d	7.75 d	7.60 t	7.58 d
	$J_{12} = 6.0$ Hz			$J_{45} = 8.7$ Hz		$J_{67} = 9.1$ Hz	$J_{78} = 7.1$ Hz	
4i	5.87 s		7.42 d	8.00 d	–	–	8.00 d	7.42 d
			$J_{34} = J_{78} = 7.6$ Hz				$J_{78} = J_{34} = 7.6$ Hz	
5i	5.92 s		7.4 d	7.98 d	–	–	7.98 d	7.4 d
			$J_{34} = J_{78} = 7.7$ Hz				$J_{78} = J_{34} = 7.7$ Hz	
4j	5.9 s		7.5 d	7.69 d	–	–	7.69 d	7.5 d
			$J_{34} = J_{78} = 7.6$ Hz				$J_{78} = J_{34} = 7.6$ Hz	
5j	5.96 s		7.49 d	7.68 d	–	–	7.68 d	7.49 d
			$J_{34} = J_{78} = 7.8$ Hz				$J_{78} = J_{34} = 7.8$ Hz	
4k	5.96 s		7.82 d	8.41 d	–	–	8.41 d	7.82 d
			$J_{34} = J_{78} = 7.7$ Hz				$J_{78} = J_{34} = 7.7$ Hz	

[1] Protons of the benzoyl group at C5

Bromination of **3a**,**b**

The reaction was carried out at 0–6°C (12–15°C in 1,4-dioxane). A solution of 0.035 ml ($6.8 \cdot 10^{-4}$ mol) of bromine in 1 ml of the appropriate solvent was poured into a precooled solution of 0.1 g of **3a** in 5 ml of the same solvent. 0.023 ml ($4.5 \cdot 10^{-4}$ mol) of bromine were used for the bromination of 0.1 g of **3b**. Due to the low solubility of **3a**,**b** in acetonitrile and nitromethane, 15 ml of solvent was used in these cases. After 30 min the solvent was evaporated without heating and the residue was analyzed.

Determination of the diastereomeric ratio (**5a/4a** *and* **5b/4b**) *from the bromination of* **3a** *and* **3b**

A sample of the reaction mixture from **3a** in *i*PrOH (5 ml of a 5 to $7.1 \cdot 10^{-4}$ *M* solution) and *i*PrOK in *i*PrOH (5 ml of a 7 to $10 \cdot 10^{-4}$ *M* solution) are mixed in a 25 ml volumetric flask, stirred, and diluted with *i*PrOH to 25 ml total volume. Within 1 min, the absorbance is measured at $\lambda = 346$ nm. This value (A_{cis}) corresponds to the amount of 1-bromoacenaphthylene formed by elimination from **5a** exclusively. Another sample of the diastereomeric mixture in *i*PrOH (5 ml as above) and *i*PrOK (5 ml of a $1–1.5 \cdot 10^{-2}$ *M* solution) are combined in a 25 ml flask which is heated at 80±2°C for 30 min. The mixture is diluted to 25 ml and the absorbance is measured. This absorption corresponds to the 1-bromoacenaphthylene formed from both stereoisomers **4a** and **5a** ($A_{cis+trans}$). The percentage of **5a** is obtained as $(A_{cis}/A_{cis+trans}) \cdot 100$. A similar procedure applies for the analysis of the bromination products of **3b** using the absorption at 353.5 nm. UV spectrum of 1,5(or 6)-dibromoacenaphthylene: λ_{max} (lgε) = 323 (4.02), 329.2 (4.05), 337.6 (3.98), 347.5 (3.81), 353.4 (3.82) nm.

General procedure for the bromination of **3a–k** *in dioxane*

1 ml of a solution of bromine (0.575 ml (0.011 mol) of bromine in 40 ml of dioxane) was added to a solution of $2.5 \cdot 10^{-4}$ mol of acenaphthylene in dioxane (3 ml) and precooled to 12°C. The mixture was allowed to stand for 30 minutes at 12–15°C (for nitroderivatives **3f**,**g**,**k**: 2–3.5 h). Then the solvent was evaporated, and the residue was analyzed by ^{1}H NMR spectroscopy.

Preparation of cis-1,2-dibromoderivatives **5a**-**g**,**i**,**j**; *general procedure*

A solution of the corresponding acenaphthylene (**3a–g**,**i**,**j**) in dioxane and a solution of Br_2 (0.1 *M* in dioxane) are combined and allowed to react at 12–15°C. The solvent is evaporated *in vacuo* without heating. For the individual conditions see Table 3; the ^{1}H NMR spectra of new compounds are given in Table 4.

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