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Introduction

Spirochromenes have been studied very actively in the past, since many of them are photochromic owing to a C(sp^3)–O bond opening reaction [2]. The thermal behaviour of these compounds has received less attention, probably because thermochromism has been encountered less frequently and was considered to be less spectacular. The only barriers for reversible ring opening have been reported for some spiro[chromene-2,2′-indolines] [3] and spiro[chromene-2,1′-(2)-oxaindans] [4]. In both cases, diastereotopic groups were a prerequisite for variable-temperature ^{1}H-NMR measurements. However, this would not be necessary if separated enantiomers were available to be racemized, in order to determine their barriers for ring opening. For instance, 2,2′-spirobichromenes (*Scheme*) might be studied in this way. Indeed, *Okamoto et al.* [5] resolved some bridged diaza derivatives of this series by HPLC on (+)-poly(tritylmethacrylate)/SiO$_2$. However, they did not detect thermal racemizations [5]. Therefore, we intended to separate the enantiomers of simpler 2,2′-spirobichromenes (*Scheme*) and to determine their barriers for ring opening.

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Scheme

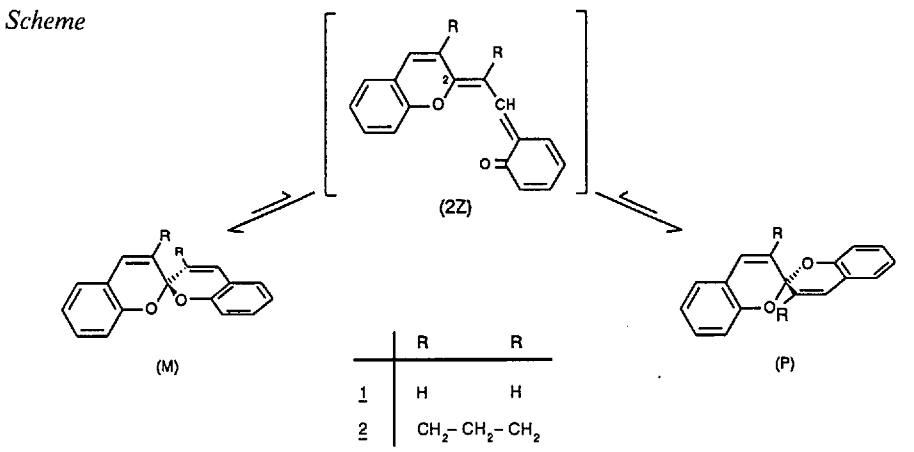

Table 1. *Properties of Enantiomers of 2,2′-Spirobichromenes. k′*: Capacity factors upon liquid chromatography on triacetylcellulose [7] (TAC) at 20° and 2 bar in EtOH/H_2O, 96:4 ($k' = 0$ for 1,3,5-tri(*tert*-butyl)benzene) and tribenzoylcellulose [8] [9] (TBC) at 22° and 33 bar in MeOH ($k' = 0$ for benzene-1,3,5-triol). *P*: Enantiomeric purity, determined by anal. HPLC at 10°. $[\alpha]^{22}$: Specific rotation in MeOH(1) or $CHCl_3$(2), calculated for $P = 100\%$

	k′		M.p. [°C]	P [%]	$[\alpha]^{22}_{365}$ (±300)	$[\alpha]^{22}_{578}$ (±50)
	TAC	TBC				
(+)-**1**	2.7	3.5	96–98	96	+ 3100	+ 450
(−)-**1**	3.2	5.7	97–99	96	− 3100	− 450
(+)-**2**	1.7	4.5	156–157	73	+ 4350	+ 620
(−)-**2**	0.9	5.0	155–157	73	− 4350	− 660

Behaviour upon Analytical HPLC

2,2′-Spirobichromene (*MP*)-**1** [6] shows separation of its enantiomers on triacetylcellulose [7] in analogy [1] to some spiro[chromene-2,1′-(2)-oxindans]. This separation is much better (*Table 1*) on the recently introduced sorbent tribenzoylcellulose [8] [9]. When the column temperature is gradually increased from 22°, photometric detection shows the 'plateau' between the two peaks which is typical [10] [11] for racemization during HPLC. When the flow rate of the eluent is diminished (*e.g.* at 45°, *Fig., a, b, c*, interrupted lines), the extent of racemization after separation increases as expected. The corresponding polarimetric detections (*e.g. Fig., a, b, c*, full lines) are in agreement with the above explanation. This is also true for the computer deconvoluted curves (*e.g.* $\alpha(V)$ in *Fig., d*). Since our deconvolution procedure [11] [12] does not require any *a-priori* peak-shape function but uses the experimental chromatograms $A(V)$ and $\alpha(V)$, exclusively, such deconvoluted curves show the relative concentrations of the enantiomers as separate functions of the retention volume *V*. The $(CH_2)_3$-bridged derivative (*MP*)-**2** [15] (*Scheme*) showed somewhat better separation by triacetyl- than by tribenzoylcellulose (*Table 1*). On the first sorbent, the whole HPLC behaviour of (+)- and (−)-**2** was similar to that shown in the *Figure*.

Barrier for Racemization during HPLC of (±)-1

Determination of 'enantiomerization' rate constants from gas chromatograms has been described by *Schurig* and coworkers [14]. *Veciana* and *Crespo* [16] [18] were the first to use the theoretical approach of *Kramer* [19] for some successful simulations in HPLC. We applied this approach [19] to (±)-**1**. For instance, the chromatogram shown in the *Figure, c*, was reproduced (*Fig., e*) by the following parameters (first number for (+)-, second one for (−)-**1**): retention volumes 26.8 and 37.1 ml and peak widths 1.3 and 1.7 ml in the absence of racemization; flow rate 0.5 ml/min; scale factors of absorbance and rotation angle; rate constants [13] 1.9 and 1.5×10^{-4} s^{-1} for ring opening. These parameters are consistent with the ones used for other flow rates (*Fig., a, b*) and temperatures, which means a low probability for successful simulations by means of wrong sets of parameters. The corresponding $\Delta G^{\neq}$ values calculated are not as accurate as the ones measured *via* rotation angles (*Table 2*). Nevertheless, the determination of barriers to racemization during HPLC is useful for at least two reasons: *1*) For some molecules, this method is probably the *only* one which can estimate the barrier, *e.g.* in the case of low specific rotations. *2*) Rates obtained in this way by investigation of *racemates* give semiquantitative information on preparative separability and the thermal stability to be expected for separated interconvertible enantiomers.

Semipreparative Enrichment of Enantiomers

From the barriers of 100 kJ/mol (*Table 2*), we concluded that the column temperature for an enrichment of (+)- and (−)-**1**

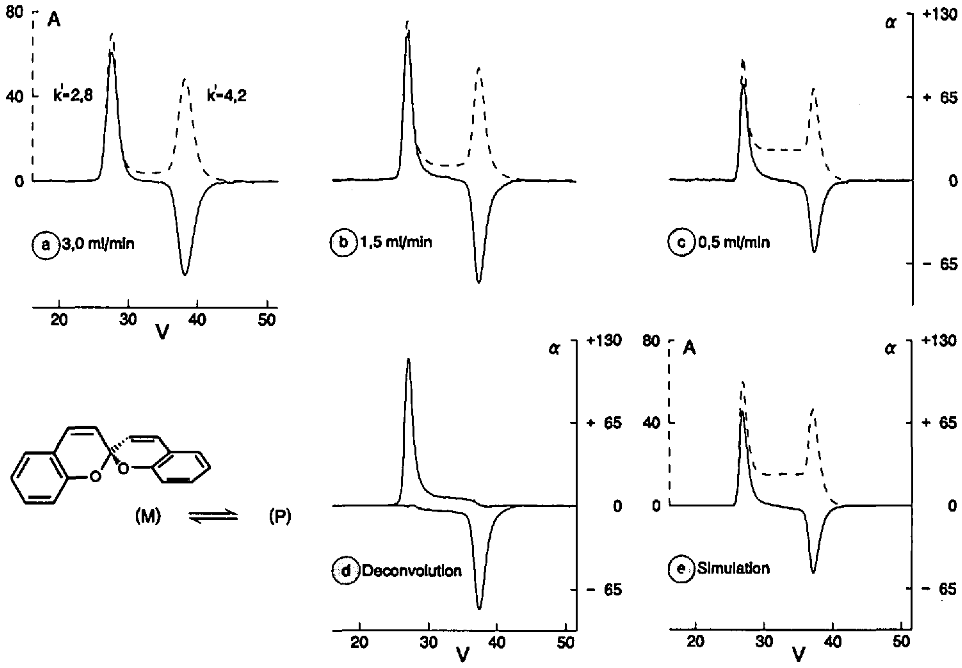

Figure. *HPLC of 0.15 mg of (MP)-***1** *in MeOH on tribenzoylcellulose* [8] [9] *at 45°. A*: Absorbance at 300 nm in arbitrary units; photometric detection as interrupted lines (– – –). α: Rotation angle at 365 nm in mdeg; polarimetric detection as full lines (–). *V*: Retention volume in ml ($V = 0$ upon injection). *k′*: Capacity factor ($k' = 0$ for benzene-1,3,5-triol). *a*) Experimental chromatograms $A(V)$ and $\alpha(V)$ at flow rate 3.0 ml/min, *b*) 1.5 ml/min, and *c*) 0.5 ml/min. *d*) Deconvoluted [11] [12] curves of the experimental chromatogram $\alpha(V)$ at 1.5 ml/min (see text), showing the relative concentration of each enantiomer as a separate function of *V*. *e*) Computer-simulated curves of the experimental chromatograms $A(V)$ and $\alpha(V)$ at 0.5 ml/min, using 1.9 and 1.5×10^{-4} s^{-1} as rate constants for ring opening (see text) [13].

Table 2. *Barriers $\Delta G^{\neq}$ for Ring Opening, Determined by Two Methods.* LC = racemization during HPLC of the racemate and subsequent computer simulation of the chromatogram (see text); ROT = racemization of a preparatively enriched enantiomer, monitored by the time-dependent rotation angle at 365 nm. *F*: Flow rate of eluent. *k*: Rate constant. For the LC method, *k* and $\Delta G^{\neq}$ represent mean values (see text) [13]; by simulation, errors between 0.5 and 1.0 kJ/mol for $\Delta G^{\neq}$ were estimated, depending upon the height of the 'plateau'.

	R	R	Solvent	Method	*T* [°C]	*F* [ml/min]	$k \times 10^4$ [s^{-1}]	$\Delta G^{\neq}$ [kJ/mol]
1	H	H	MeOH	LC	45	0.5	1.7	101
			MeOH	LC	45	1.5	2.1	100
			MeOH	LC	45	3.0	2.5	100
			MeOH	ROT	45.0	–	3.69	99.0 ± 0.2
			MeOH	LC	35	1.5	0.6	100
			Diglyme	ROT	40.0	–	0.24	104.5 ± 0.2
2	CH_2–CH_2–CH_2		Diglyme	ROT	45.8	–	0.47	104.7 ± 0.3

should be 22°, if proper fractions were cut, and that the temperature for their collecting and subsequent analyzing the sample should not be higher than 10°. Determinations of enantiomeric purities (*Table 1*) were performed on tribenzoylcellulose as described in [8] [9]. This sorbent turned out to be useful for preparative work as well (particle sizes 20–30 µm, column 300 × 25 mm, pressure 2.1 bar, flow rate 4.3 ml/min). Similar conditions were used for (+)- and (−)-**2** [20] on triacetylcellulose (*Table 1*).

Barriers for Racemization of Preparatively Enriched Enantiomers

UV absorption of **1** and **2** occurs at λ_{max} < 330 or 315 nm, respectively. Our racemizations (*Table 2*) were monitored at 365 nm in an otherwise dark polarimeter. Therefore, our values do not contain contributions from irradiation but represent *thermal* reactions. When **1** or **2** is heated to 78° in EtOH or to 150° in DMF, no colour is visible. Therefore, any ring-opened molecules must be short-lived, *i.e.* intermediates of high free enthalpy. The $(CH_2)_3$ bridge in **2** effects that no intermediate can attain a (2*E*)-stereostructure but should have the (2*Z*) one (*Scheme*). The barrier for ring opening of **2** is very similar to the barrier determined for **1** (*Table 2*) which probably means that any intermediate of the racemization of **1** has the (2*Z*)-stereostructure, too. The latter is of course stabilized by resonance (although we did not include the corresponding dipolar formula into the *Scheme*). Since the (*E*)- or (*Z*)-relationships with respect to the *other* partial double bonds are not known, our formula (*2Z*) does not answer these details. Although statistical factors might take into account the intermediate(s) and also the *two* $C(sp^3)$–O bonds in one molecule to be opened, we decided to list only non-corrected rate constants and barriers (*Table 2*). These values cannot yet be compared with the known ones [3] [4], determined by ^{1}H-NMR of diastereotopic groups, because of the differing substitution patterns. In the future, the structural factors governing reversible opening of spirochromenes can, in addition, be investigated by thermal racemization of preparatively enriched enantiomers, a method which had not yet been applied to 2*H*-pyrans. The optically active compounds may also serve to study *photochemical* racemizations which, up to now, were possible only in the few cases [1] [5] where separations had been performed.

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