

ENANTIOMERS OF POLARIZED ALKENES:
 CHROMATOGRAPHIC ENRICHMENT AND THERMAL INTERCONVERSION^{1,2)}

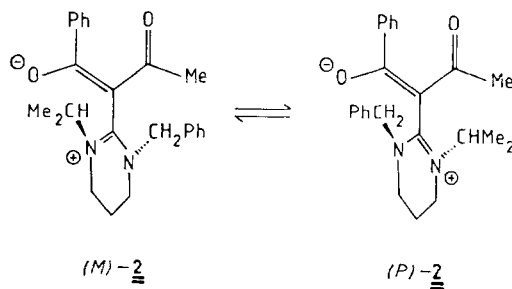
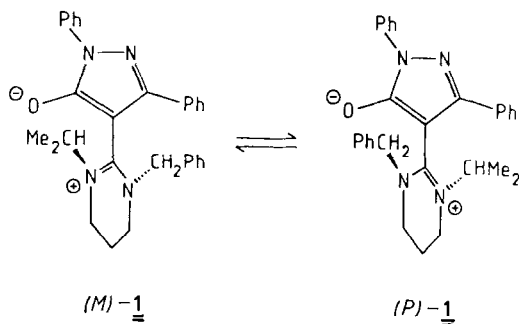
U. Berg^{a)}, R. Isaksson^{a,b)}, J. Sandström^{a)}, U. Sjöstrand^{a)},
A. Eiglsperger^{b)}, and A. Mannschreck^{b)*)}

a) Division of Organic Chemistry 3, Chemical Center, University
 of Lund, P.O.B. 740, S-22007 Lund, Sweden

b) Institut für Organische Chemie, Universität Regensburg, Universi-
 tätsstrasse 31, D-8400 Regensburg, Germany

*(+)- and (-)-1 as well as (+)- and (-)-2 were partially separated
 by liquid chromatography on triacetylcellulose; racemizations resulted
 in the barriers (Table 2) to rotation via planarized transition states.*

It has previously been shown⁵⁻⁷⁾ that push-pull ethylenes with
 strong donor groups on C¹, strong acceptor groups on C², and suffi-
 ciently strong steric interaction between the two halves of the
 molecule are twisted in solution. Therefore, the ground states of
 $\underline{1}$ ^{8,9)} and $\underline{2}$ ¹⁰⁾ will consist of two non-coplanar parts: A negatively



charged "enolate" part and a positively charged "amidinium" part, each being represented above by a single resonance formula only. (The formulae of 2 give an arbitrary stereostructure for its "enolate" part). In 1 and 2 the barriers to partial rotation (M) \rightleftharpoons (P) about the central C-C bond have been determined by ^1H NMR lineshape analysis to 101 kJ mol^{-1} (174°C)⁸⁾ and 97 kJ mol^{-1} (139°C)¹⁰⁾, respectively, both in o-dichlorobenzene.

Since the exchange process has been shown to have a positive activation entropy (28 to $43 \text{ J mol}^{-1} \text{ K}^{-1}$) in similar systems⁶⁾, the racemization of the enantiomers of 1, 2, and similar compounds should be sufficiently slow for resolution at room temperature⁸⁾. The present paper reports the first partial separations of the enantiomers of polarized alkenes.

These were accomplished for (+)- and (-)-1 as well as for (+)- and (-)-2 by semipreparative liquid chromatography (LC)¹¹⁾ on microcrystalline, swollen triacetylcellulose using low pressure, because this procedure has proven successful with other twisted π -systems^{3,12)}. The chemical purity of the collected samples (Table 1) was confirmed by ^1H NMR. Addition of (*S*)-1-(9-anthryl)-2,2,2-trifluoroethanol to an enriched sample of (+)-1 causes further doubling of the four ^1H NMR signals for the diastereotopic CH_3 groups in $-\text{CHCH}_3^1\text{CH}_3^2$ ($\delta(\text{CH}_3^1) = 1.22$, $\delta(\text{CH}_3^2) = 0.68$, $^3J_{\text{HH}} = 6.7 \text{ Hz}$) by the formation of diastereomeric association complexes. The enantiomeric purity *P* of this sample was determined by integration of the unequal intensities of the two CH_3^1 doublets in the presence of the auxiliary. *P* resulted in $[\alpha]_{546}^{25} = 24^\circ_{\text{m}}$

Table 1. Enriched enantiomers of 1 and 2; (+)-enantiomers eluted first.

	$w^a)$	M.p.	$[\alpha]_{\lambda}^{25b)}$	λ	$c^c)$
	[mg]	[$^\circ\text{C}$]	[$^\circ \text{ ml g}^{-1} \text{ dm}^{-1}$]	[nm]	[g l $^{-1}$]
(+)- <u>1</u>	20	171.5-174.5	$+ 3.3 \pm 0.4^d)$	546	8.5
(+)- <u>2</u>	19	185.5-187.5	$+11.8 \pm 1.0$	436	3.4
(-)- <u>2</u>	20	186.0-187.5	-10.0 ± 0.6	436	6.0

a) Approximate weights of fractions, collected after LC (see text) of 67 mg of racemate.

b) Specific rotations in EtOH

c) Concentrations of $[\alpha]$ measurements.

d) Optical purity 13% (cf. text).

$\text{g}^{-1} \text{ dm}^{-1}$ (5.6 g/l EtOH) for the pure enantiomer. The determinations of P for our samples of 2 by LC³⁾ and by ^1H NMR were not yet successful. The signal-to-noise ratio of the circular dichroism of (+)-1 and (+)-2 was too low to provide meaningful data, probably because of insufficient enrichments and/or low $\Delta\epsilon$ -values.

Our results confirm the chirality of 1 and 2; the barriers (Table 2) to partial rotation (M) \rightleftharpoons (P), obtained by first-order thermal racemizations, are compatible with the ones mentioned above, if differences in solvent and temperature are taken into account. The increase of ΔG^\ddagger for 2 when going from dioxane to ethanol can be explained by a stronger stabilization⁶⁾ by hydrogen bonds in the highly polarized non-planar ground state than in the less polar transition states with the two $\text{C}(\text{sp}^2)$ centers in *coplanar* orientation. A diastereomerization is also possible in this system, comprising a transition state with the two $\text{C}(\text{sp}^2)$ centers in *perpendicular* orientation^{13,14)}. However, in 1 and 2 the barrier to this motion is evidently much lower than the one for enantiomerization. In an analogue of 2, a twist angle of 73° between the $\text{C}(\text{sp}^2)$ planes in the crystal has been found by X-ray crystallography¹⁵⁾.

The above approach will be useful for further measurements of barriers to rotation, including the ones in different media. The chiroptical properties like circular dichroism will be of interest, e.g. for the estimation of angles of twist in the ground state of polarized alkenes.

Table 2. Barriers to partial rotation (M) \rightleftharpoons (P) about the central C-C bond (see formulae), obtained by thermal racemizations which were monitored by polarimetry.

	Solvent	T [$^\circ\text{C}$]	ΔG^\ddagger a) [kJ mol^{-1}]
(+)- <u>1</u>	EtOH/H ₂ O, 96:4	69.5	109.7 ± 0.3
(+)- <u>2</u>	Dioxane, abs.	34.6	95.4 ± 0.2
(-)- <u>2</u>	EtOH/H ₂ O, 96:4	57.7	107.2 ± 0.3

a) Calculated by means of a computer program¹⁶⁾ from the decrease of the rotation angle during 1.5 half-lives.

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*) Author to whom correspondence should be addressed.

- 1) Liquid Chromatography on Triacetylcellulose, Part 5. - Part 4: Ref. 3.
- 2) Studies of Polarized Ethylenes, Part 13. - Part 12: Ref. 4.
- 3) A.Mannschreck, A.Eiglsperger, and G.Stühler, *Chem.Ber.* 115, 1568 (1982), and references cited therein.
- 4) J.Sandström and I.Wennerbeck, *Acta Chem.Scand.* B32, 421 (1978).
- 5) U.Sjöstrand and J.Sandström, *Tetrahedron* 34, 3305 (1978), and references cited therein.
- 6) U.Berg and U.Sjöstrand, *Org.Magn.Reson.* 11, 555 (1978).
- 7) Review: J.Sandström, *Topics Stereochem.* (1982).
- 8) U.Sjöstrand, Ph.D. Thesis, University of Lund 1977, p. 19, 22.
- 9) 1, m.p. 109-110°C.
- 10) J.Sandström and U.Sjöstrand, *Tetrahedron* 34, 371 (1978).
- 11) H.Häkli, M.Mintas, and A.Mannschreck, *Chem.Ber.* 112, 2028 (1979).
- 12) G.Becher and A.Mannschreck, *Chem.Ber.* 114, 2365 (1981); M.Wittek, V.Vögtle, G.Stühler, A.Mannschreck, B.M.Lang and H.Irngartinger, *Chem.Ber.*, submitted for publication; A.Mannschreck, A.Talvitie, W.Fischer, and G.Snatzke, *Monatsh.Chem.*, submitted for publication.
- 13) J.Sandström, U.Sjöstrand, and I.Wennerbeck, *J.Am.Chem.Soc.* 99, 4526 (1977).
- 14) Review: H.-O. Kalinowski and H.Kessler, *Topics Stereochem.* 7, 295 (1973).
- 15) D.Adhikesavalu and K.Venkatesan, personal communication, quoted in Ref. 7.
- 16) U.Kölle, B.Kolb, and A.Mannschreck, *Chem.Ber.* 113, 2545 (1980).

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