Short Communication

Asymmetric photochemistry: transfer of optical activity from educt to product in the photolysis of *trans*-3,5-diphenylpyrazoline with circularly polarized light

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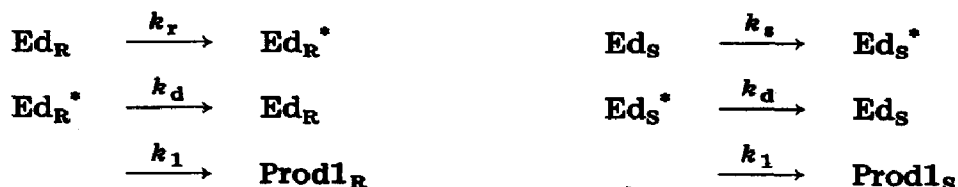*Institut für Chemie, Universität Hohenheim, D-7000 Stuttgart 70 (F.R.G.)*
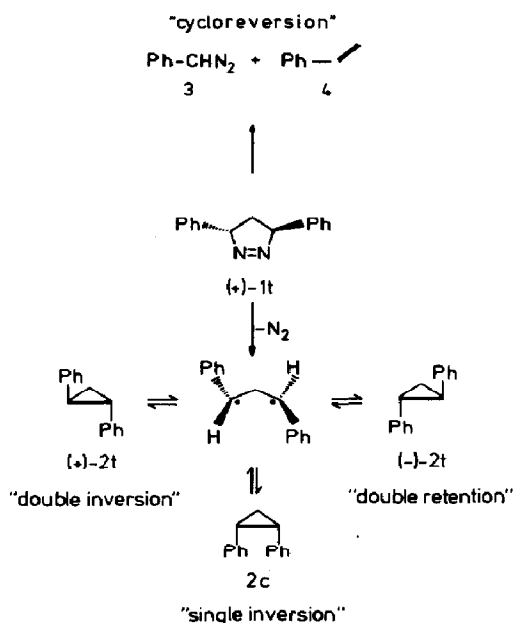
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Reports on asymmetric photochemistry employing racemic mixtures of optically active molecules and circularly polarized light (CPL) have mostly focused attention on the optical activity created in the educt remaining after incomplete photolysis [1]. In this paper the optical activity of the product is of prime interest. The degree of transfer of optical activity from educt to product has been used to obtain information about mechanistic questions. In general, resolved enantiomers have been used [2 - 5]. We show in this paper that the much simpler method of CPL photolysis of the racemate can give the same information.

The photolysis of *trans*-3,5-diphenylpyrazoline (1t) involves a cyclo-reversion and a "biradical" pathway [6, 7]. Scheme 1 contains the formally possible processes of biradical stabilization for one enantiomer, *e.g.* (+)-1t. Product analysis should allow discrimination between these pathways.

In our experiments we do not start from the pure enantiomer; resolution and photolysis are performed simultaneously. The kinetic principles of this independent parallel reaction of the enantiomers have been presented elsewhere [1]. The educt becomes optically active since one enantiomer is photolysed more rapidly than the other. If an optically active molecule is formed in the reaction, 2t in Scheme 1, and if there is some conservation of optical activity, then the optical purity $P = (c_R - c_S)/(c_R + c_S)$ of the product will be connected to the optical purity of the educt.

If we assume that the differential absorption of CPL by the enantiomers (k_r and k_s) is the only asymmetric step in the reaction sequence

$$Ed_R \xrightarrow{k_r} Ed_R^*$$

$$Ed_R^* \xrightarrow{k_d} Ed_R$$

$$\xrightarrow{k_1} Prod1_R$$

$$Ed_S \xrightarrow{k_s} Ed_S^*$$

$$Ed_S^* \xrightarrow{k_d} Ed_S$$

$$\xrightarrow{k_1} Prod1_S$$

Scheme 1. The formally possible processes of biradical stabilization for (+)-1t.

and if we further assume that total transfer of optical activity from educt to product occurs, then we can solve the rate equations for the products:

$$c_R(\text{Prod1}) = \frac{k_1}{\sum k_i}\{c_R(\text{Ed}) - c_0\}$$

and

$$c_S(\text{Prod1}) = \frac{k_1}{\sum k_i}\{c_S(\text{Ed}) - c_0\}$$

where c_0 is the initial concentration of each of the educt enantiomers. So we obtain

$$P(\text{Prod1}) = \left|\frac{c_R(\text{Prod1}) - c_S(\text{Prod1})}{c_R(\text{Prod1}) + c_S(\text{Prod1})}\right|$$

$$= \left|\frac{c_R(\text{Ed}) - c_S(\text{Ed})}{c_R(\text{Ed}) + c_S(\text{Ed}) - 2c_0}\right|$$

which is independent of the number of non-asymmetric side reactions. This calculated optical purity can be compared with that determined experimentally from circular dichroism (CD) and UV spectroscopic measurements.

The irradiation equipment has been described elsewhere [1]. (+)-CPL irradiation of stirred solutions of (±)-1t (approximately 10^{-3} M) at 330 ± 7.5 nm was used to determine the chiroptical data for the educt and the

TABLE 1

Optical and CPL photolysis data for 1t

Solvent	ϵ_{330} (l mol^{-1} cm^{-1})	$[\theta]_{330}$ (deg cm^2 dmol^{-1})	$g_{330} \times 10^2$	P_{rel}[a] at 63%	κ
Hexane	306	62 000	6.14	0.99	1.064
Benzene	370	79 000	6.43	1.03	1.066
α-Pinene	306	68 000	6.76	1.06	1.070
Ethanol	310	82 000	7.81	1.23	1.082
Acetonitrile	314	90 000	8.63	1.34	1.090

[a]$P_{rel} = (c_R - c_S)/2c_0$ at $\zeta = 0.63$, where ζ is the extent of reaction.

asymmetry $\kappa = k_s/k_r$ of the reaction in various solvents (Table 1), as has been reported previously [1]. In the experiments to determine transfer of optical activity the irradiation was terminated at about 63% completion of the reaction for analysis of the products. The UV and CD spectra of the reaction mixture around 330 nm are solely due to 1t; thus with the data of Table 1 P(1t) and P(2t) for 100% transfer could be calculated. The absorption at 308 nm is due both to 1t and to 3 the absorption coefficient of which is known. From the data at 330 and 308 nm the concentration of 3 and the weight of the cycloreversion pathway were determined. 2c and 2t were jointly separated from the other products of the reaction mixture by thin layer chromatography with 1:1 ethanol–ether and were eluted from the silica using hexane. Their individual concentrations were determined from the absorbance of the eluate at 276 nm (Zeiss DMR 10 spectrophotometer; $\epsilon_{2t} = 1010$ l mol^{-1} cm^{-1}; $\epsilon_{2c} = 285$ l mol^{-1} cm^{-1}) and from the ratio of the integrated areas of the gas chromatography or high pressure liquid chromatography peaks (this ratio is 0.10 - 0.15 except for benzene where it approaches 0.30). The CD spectrum (Jasco 500 spectropolarimeter) of the eluted solution is characteristic of 2t ($[\theta]_{276} = 17\,000$ deg cm^2 dmol^{-1} in hexane). Of course we lost some material during this procedure which lowered the CD values considerably. We therefore conservatively estimate 30% uncertainty in the experimental value of P(2t).

The results presented in Table 2 indicate that in most solvents a high amount of optical activity is transferred from 1t to 2t.

The signs of the CD bands of 1t and 2t allow discrimination between double inversion and double retention. (+)-CPL irradiation leads to a negative CD value at 330 nm which can be related to $(3S,5S)$-1t by application of an octant rule for cis-azo compounds [8]. This means that $(3R,5R)$-1t is preferentially destroyed. We observe negative CD bands of 2t at 276, 268, 262 and 230 nm which are related to $(1S,2S)$-2t [9]. This indicates double retention. Our findings are in agreement with other work [5] that has been performed with resolved enantiomers and it supports the proposal of Inagaki and Fukui [10] of a configurationally stable intermediate. However, in benzene any conformational information is lost

TABLE 2

Transfer of optical activity from 1t to 2t

Solvent	ζ	$P_{en}(calc)$ (%)	$P_{en}(exp)$ (%)	ϕ (%)
Hexane	0.66	1.51	1.50	100 ± 15
Benzene	0.63	1.60	—	0
α-Pinene	0.45	1.96	1.92	98 ± 30
Ethanol	0.72	1.57	2.02	130 ± 30
Acetonitrile	0.73	1.70	1.91	112 ± 30

((+)-2t, (—)-2t and 2c are comparable in concentration). We cannot offer an interpretation for this at present.

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