ppm must therefore belong to the lithiated carbons of the "outer" ligands, while that at 188.45 corresponds to these carbons in the "inner" ligand. On the other hand, from the two ^{6}Li signals, the high field one belongs to the "inner" and the low field one to the "outer" lithium site. Each C,Li contact is thus formally a three-center two-electron bond.

The new experiment described here further supports our conclusions drawn from the results of the homonuclear ^{6}Li,^{6}Li COSY experiment[6] since it shows independently that the two lithium NMR signals of **1** belong to different lithium sites in the *same* cluster. ^{6}Li,^{13}C shift correlations of the type presented here are thus a valuable addition to the arsenal of NMR techniques used for structure elucidations of lithium–organic compounds in solution.

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Stereocontrol by Energy Transfer: Photoisomerization of α-Arylalkyl Spiro[cyclopropane-1,9′-fluorene]-2-carboxylate

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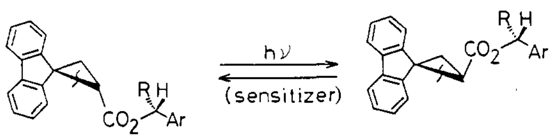
Stereocontrol by selective energy transfer is an attractive subject in photochemistry. Hammond and Cole reported asymmetric induction in the cis-to-trans isomerization of 1,2-diphenylcyclopropane with use of a chiral sensitizer.[1] The reaction was also investigated by Ouannès[2] and more recently by Horner.[3] The origin of the stereodifferentiation must be directly related to the conformational factors in the exciplex or the encounter complex involved in the energy transfer step. However, such factors have been little considered because of conformational freedom of the complex and the poor optical yields obtained (less than 10%). Highly diastereoselective photoreactions controlled by selective energy transfer in models with reasonable conformational flexibility have not yet been reported.

We have recently reported an asymmetric transformation of *N*-(*R*)-(+)-α-arylethyl spiro[cyclopropane-1,9′-fluorene]-2-carboxamide derivatives,[4,5] in which the key step of the diastereodifferentiation is deduced to be in the energy-transfer step. We now wish to report, with clear-cut evidence, highly diastereoselective isomerization controlled by the rate of energy transfer by using intramolecular sensitization of α-phenanthrylalkyl spiro[cyclopropane-1,9′-fluorene]-2-carboxylate (**4Aa–c** ⇄ **4Ba–c**).

As previously reported, the photoracemization of methyl spiro[cyclopropane-1,9′-fluorene]-2-carboxylate (**1**) proceeds via triplet sensitization with high quantum yield (0.88 for acetophenone sensitization).[4] Transformation of diasteromeric esters having an α-arylethyl group, **2A(B)** or **3A(B)**, is also sensitized by various sensitizers. Diastereomeric ratios at the photostationary state are as follows:[6] (**2A**:**2B**, 52:48 for acetophenone; **3A**:**3B**, 81:19 for acetophenone (E_T 73.7 kcal/mol); 82:18 for *p*-methoxyacetophenone (E_T 71.8); 83:17 for triphenylene (E_T 66.5); 92:8 for phenanthrene (E_T 61.9); 93:7 for *p*-phenylacetophenone (E_T 61.1). These can be summarized as follows: (1) Moderate-to-high selectivity for **3A(B)** and poor selectivity for **2A(B)** are observed. (2) The selectivity becomes higher when the triplet energy of sensitizers becomes lower. These results are best explained by a consecutive energy-transfer mechanism involving an intramolecular process (sensitizer → naphthyl → fluorenyl) (Scheme I).

Scheme I



2A,3A,4Aa~c   2B,3B,4Ba~c

2A(B); R = Me, Ar = Ph
3A(B); R = Me, Ar = 1-naphthyl
4A(B)a; R = Me, Ar = 9-phenanthryl
4A(B)b; R = Et, Ar = 9-phenanthryl
4A(B)c; R = *i*-Pr, Ar = 9-phenanthryl

Table I. Photoisomerization of **4A(B)a–c** and the Kinetic Parameters[a]

compd	isomer ratio[b]	quantum yield[c]	$k_1 \times 10^{-4}$ (s^{-1})
4Aa	92:8	0.17 (**4Aa** → **4Ba**)	2.9 ± 0.2
4Ba		0.40 (**4Aa** ← **4Ba**)	77 ± 4
4Ab	94:6	0.094 (**4Ab** → **4Bb**)	1.9 ± 0.1
4Bb		0.40 (**4Ab** ← **4Bb**)	88 ± 5
4Ac	97:3	0.086 (**4Ac** → **4Bc**)	0.92 ± 0.05
4Bc		0.40 (**4Ac** ← **4Bc**)	73 ± 4

[a] At room temperature in benzene under argon atmosphere (>310 nm for flash photolysis, 355 nm for laser photolysis). [b] **4Aa–c**:**4Ba–c** at [**4Aa–c** plus **4Ba–c**] = 1.2 × 10^{-3} M, determined by HPLC. [c] At 334-nm excitation using potassium ferrioxalate actinometer.

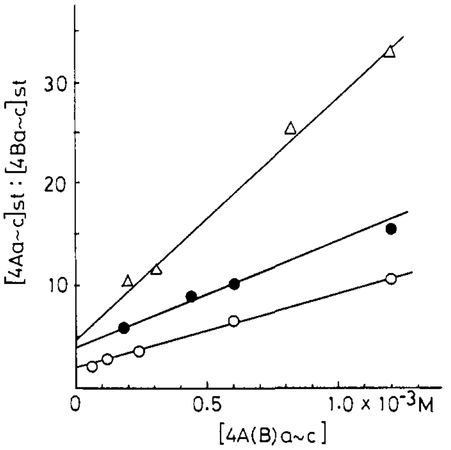


Figure 1. Concentration effect on the photoisomerization of **4Aa–c** ⇄ **4Ba–c** at room temperature in benzene under argon atmosphere [(○) for **4A(B)a**; (●) for **4A(B)b**; (△) for **4A(B)c**].

To demonstrate selective intramolecular energy transfer mechanism, we have investigated the isomerization of **4Aa–c** ⇄ **4Ba–c** in which the substrates have a 9-phenanthryl group on the asymmetric carbon in the ester group. Selective excitation (>310 nm) of the phenanthryl group, without added sensitizer, leads to the photostationary state. Table I shows the diastereoisomer ratios at the photostationary state as well as the quantum yields.[6] The same ratio was obtained whether one starts from pure diastereomer or from the mixture of **4Aa–c** and **4Ba–c**. The observed high diastereoselectivity (84% de for **4A(B)a**; 88% de for **4A(B)b**; 94% de for **4A(B)c**) is in accordance with the fact that the intramolecular sensitization is a key step in the isomerizations.

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[1] Hammond, G. S.; Cole, R. S. *J. Am. Chem. Soc.* **1965**, *87*, 3256.
[2] Ouannès, C.; Beugelmans, R.; Roussi, G. *J. Am. Chem. Soc.* **1973**, *95*, 8472.
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[5] Okada, K.; Samizo, F.; Oda, M.; Harada, N.; Uda, H. *Tetrahedron Lett.* **1986**, *27*, 4493.
[6] Stereochemistries of the diastereomers are determined as depicted in the text; see ref 5.

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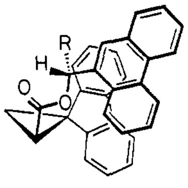
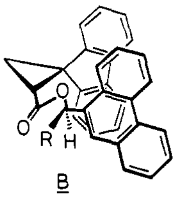
For estimation of the rate of energy transfer from the phenanthryl to the fluorenyl group, the triplet decay of the phenanthryl group in **4Aa–c** and **4Ba–c** was measured by means of flash and laser photolyses. From the observed decay curves, the first- and the second-order rate constants can be distinguished by the concentration dependence of the decay. The first-order rate constants (k_1, Table I[7]) are remarkably different between the diastereomers (k_1(**4Ba–c**)/k_1(**4Aa–c**): 27 for R = Me, 46 for R = Et, 79 for R = *i*-Pr), strongly suggesting that the rate of intramolecular energy transfer from the phenanthryl to the fluorenyl moiety is much faster in **4Ba–c** than in **4Aa–c**. This can be rationalized by the conformational models A and **B**. Triplet energy transfer, which is widely thought to occur via an electron exchange mechanism, from the phenanthryl to the fluorenyl group requires an orbital overlap[8] of these chromophores. Such an overlap is easily achieved in **B** but not in A owing to steric repulsion between the alkyl and the fluorenyl groups.[9,10] As a consequence, **4Aa–c** is photochemically less reactive than **4Ba–c**. The second-order decays of the triplet excited states, which are in the range of 1–3 × 10^6 M^{-1} s^{-1} for **4Aa–c** and 10–50 × 10^6 M^{-1}/s^{-1} for **4Ba–c**,[7] are interpreted as intermolecular energy transfers from the phenanthryl to the fluorenyl moiety.



A



B

It is interesting to note from Table I that the photostationary state ratio of **4Aa–c**:**4Ba–c** largely deviates from the ratio expected from the quantum yields of **4Aa–c** and **4Ba–c**. This is due to isoenergetic intermolecular energy transfer between the phenanthryl groups from **4Aa–c**, having the longer triplet life time, to **4Ba–c**, which more rapidly isomerizes to **4Aa–c** after the above mentioned intramolecular energy transfer. As a result, the diastereoselectivity is concentration dependent (Figure 1). The higher the concentration, the higher the stereoselectivity. The intercept (1.8 ± 0.1 for **4A(B)a**, 4.5 ± 0.3 for **4A(B)b**, 5.5 ± 0.9 for **4A(B)c**) at 0 M of the substrate is close to the ratio of quantum yields.

In summary, we have demonstrated that the triplet lifetime of the phenanthryl group of **4Ba–c** is 30–80 times shorter than that of **4Aa–c**. Since these values are large enough to account for the diastereoisomeric ratio at the photostationary state (2–33 at the concentration up to 1.2 × 10^{-3} M which is close to the saturation limit), we conclude that the diastereodifferentiation mainly operates in the energy-transfer step. Large concentration effect on the diastereoselectivity also supports this conclusion. More detailed studies including temperature effects and asymmetric synthesis with use of chiral α-arylalkyl groups will be published in a full paper.

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[7] The second-order rate constants (k_2) are as follows: (k_2 × 10^{-6} M^{-1} s^{-1}) 2.2 ± 1.1 for **4Aa**, 42 ± 13 for **4Ba**, 1.4 ± 0.7 for **4Ab**, 18 ± 5 for **4Bb**, 2.6 ± 1.3 for **4Ac**, 27 ± 8 for **4Bc**. These data suggest that the intramolecular energy transfer from the phenanthryl group to the spirocyclopropanefluorene moiety is endothermic in the extent of 3~5 kcal/mol; triplet energy of spirocyclopropanefluorene moiety will be about 65–67 kcal/mol.

[8] Turro, N. J. *Modern Molecular Photochemistry*; Benjamin-Cumming, Menlo Park, CA, 1978; pp 305–309.

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[10] The ^{1}H resonance of the methyl protons of **4Aa–c** (δ in $CDCl_3$: 1.51 for **4Aa**, 0.56 for **4Ab**, 0.58 for **4Ac**) appears at higher field than those of **4Ba–c** (δ in $CDCl_3$: 1.74 for **4Ba**, 1.00 for **4Bb**, 0.98 for **4Bc**) supports these conformational models.

"Pseudoliquid" Behavior of Heteropoly Compound Catalysts. Unusual Pressure Dependencies of the Rate and Selectivity for Ethanol Dehydration

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Heteropoly compounds are now utilized as industrial catalysts for olefin hydration and aldehyde oxidation and as interesting cluster models of mixed oxide catalysts.[1]

Certain heteropoly acids, like $H_3PW_{12}O_{40}$ and $H_3PMo_{12}O_{40}$, easily absorb a large amount of water, alcohols, and ethers in the solid state, although their surface areas are very low.[2] This is not adsorption in micropores; rather molecules are absorbed between the lattice polyanions, sometimes expanding the lattice. The expansion can be seen visually as well as by X-ray diffraction. We showed that in some cases catalytic reactions take place in this novel bulk phase.[2,3] Presumably due to this behavior, very high catalytic activity and unique selectivity[4] as well as unusual reactivity order[5] have been observed. We called this state the "pseudoliquid phase". However, in only one case[3] was the amount of absorbed reactant measured under the working conditions.

We report here unusual pressure dependencies of the rate and selectivity of ethanol dehydration over heteropoly compounds. The dependency can only be explained by the formation of a pseudoliquid phase, i.e., a phase where the amount of absorbed ethanol has changed as a function of ethanol pressure.

Reactions were carried out by a conventional flow method, with 0.4–60 kPa of ethanol in He. The outlet gas was directly introduced to a quadrupole mass spectrometer and a gas chromatograph. Catalysts were $H_3PW_{12}O_{40}{\cdot}nH_2O$ (surface area: 5 m^2 g^{-1}) and a typical acidic Cs salt, $Cs_{2.5}H_{0.5}PW_{12}O_{40}{\cdot}nH_2O$ (114 m^2 g^{-1}), of which the physical and acidic properties have been described previously.[4] Prior to the reaction, these compounds were pretreated in situ in the stream of He for 1 h at 150 °C. The values of *n* after this pretreatment was close to zero.[7] It was confirmed that the rate and the composition of the products changed little during the time course of the reaction and that the selectivity was constant up to 60% conversion when the amount of catalyst was increased.

The amount of absorbed ethanol under the working conditions was directly measured by means of a transient-response method as described below.[3] At the stationary state of the reaction, the feed gas was instantaneously changed from ethanol-d_0 to -d_6, and the variation of the composition at the outlet was followed by a mass spectrometer and a gas chromatograph. The content of ethanol-d_0 plus -d_1 (C_2H_5OH and C_2H_5OD) in the outlet gas decreased and the content of C_2D_5OD plus C_2D_5OH increased, but the change occurred more slowly than in an experiment without a catalyst. The differences of these transient responses compared to the blank experiment correspond to the amounts of ethanol being absorbed under the working conditions. From the analysis of the transient-response curve, it can be further shown that the rate of absorption–desorption is much faster than the rate of dehydration.[3]

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(1) For example, see: Finke, R. G.; Rapko, B.; Saxton, R. J.; Domaille, P. J. *J. Am. Chem. Soc.* **1986**, *108*, 2947–2960. Misono, M. *Catal. Rev. Relat. Subj.*, in press.

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