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ASYMMETRIC INDUCTION VIA INTRAMOLECULAR T_2-SENSITIZATION: PHOTOISOMERIZATION OF α-(9"-ANTHRYL)ETHYL SPIRO[CYCLOPROPANE-1,9'-FLUORENE]-2-CARBOXYLATES

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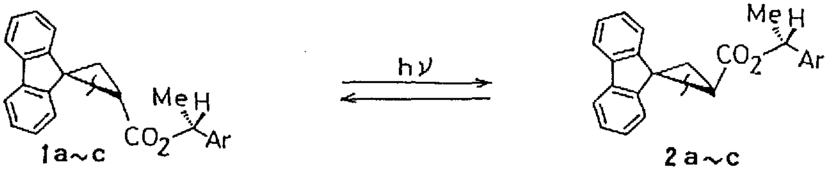
Summary: The photoisomerization of α-(9"-anthryl)ethyl spiro[cyclopropane-1,9'-fluorene]-2-carboxylates (**1c**$\rightleftarrows$**2c**) proceeds diastereoselectively through the selective intramolecular energy transfer from the second triplet state of anthryl group to the fluorenyl moiety. Asymmetric induction using optically active α-(9"-anthryl)ethyl group is achieved in high optical and chemical yields.

We have recently reported highly diastereoselective photoisomerization (**1a,b**$\rightleftarrows$**2a,b**) in which the rate of intramolecular triplet-triplet energy transfer from the phenanthryl (naphthyl) to the fluorenyl moiety controls the diastereoselectivity.[1] As can be estimated from the triplet energies of phenanthrene (62 kcal/mol) and fluorene (68 kcal/mol),[2] the above energy transfer is a little endothermic.[1] When the 9-phenanthryl group is replaced by the 9-anthryl group having a much lower triplet energy (42 kcal/mol for anthracene),[2] the intramolecular sensitization is thought hardly to occur from the lowest triplet (T_1) state of the anthryl group owing to the highly endothermic energy transfer. Furthermore, the S_1(anthryl)→S_1(fluorenyl) energy transfer is considered to be also highly endothermic process (ca. -19 kcal/mol).[2] Nevertheless, as shown in this letter, the photoisomerization proceeds in moderate quantum yields. We wish to report the diastereoselective photoisomerization of α-(9''-anthryl)ethyl spiro[cyclopropane-1,9'-fluorene]-2-carboxylates (**1c**$\rightleftarrows$**2c**), in which the selective energy transfer from the second triplet (T_2) state of the anthryl groups to the fluorenyl moiety is an origin of the diastereoselectivity; the first example of the diastereoselective isomerization via an upper excited state.

Irradiation of a diastereomeric mixture of **1c** and **2c** in benzene at room temperature under N_2 through a glass filter (>350 nm) with a 500-W Xenon lamp produced the photostationary state (**1c**:**2c** = 95:5) within 2 h. The same ratio was also observed from pure **1c** or **2c**. Table 1 shows the reaction quantum yields under N_2 and aerated conditions, and lifetimes of the S_1 and T_1 states of anthryl groups of **1c** and **2c**. As mentioned above, the S_1→S_1 and



1a~c 2a~c

Ar; a: 1-naphthyl, b: 9-phenanthryl, c: 9-anthryl

Table 1. Quantum yields of the isomerizations and lifetimes of singlet (S_1) and triplet (T_1) states of **1c** and **2c**.

compd.	quantum yield[a] (argon)	quantum yield[a] (air)	S_1 life time[b] (argon)	T_1 life time[c] (argon)	T_1 life time[c] (air)
1c	0.0019	0.0013	5.2 ns	252 μs	200 ns
2c	0.059	0.043	5.7 ns	259 μs	227 ns

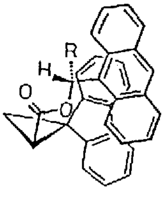
a) in benzene at r.t. at [**1c**] = [**2c**] = 1.2×10^{-3} M irradiated at 366 nm. b) determined by the fluorescence quenching by dissolved oxygen at r.t. in benzene. c) determined by the decays of T-T absorption using flash- and laser-photolyses experiments.

$T_1 \rightarrow T_1$ energy transfers from the anthryl to the fluorenyl moiety are highly endothermic processes. However, since the reaction quantum yields are not high (Table 1), the possibility of these highly endothermic processes (via nonvertical energy transfer to the spirocyclopropane-fluorene moiety if occur) is considered at first. The $T_1 \rightarrow T_1$ energy transfer can be excluded by the oxygen quenching experiment: the isomerization is quenched by dissolved oxygen to the extent of 27-32%, whereas the T_1 state of the anthryl group is almost completely quenched (to the extent of 99.9%) (Table 1). The $S_1 \rightarrow S_1$ energy transfer is also not likely to occur, since the S_1 lifetime of the anthryl groups is not short compared with that of anthracene. In more rigorous sense, the $S_1 \rightarrow S_1$ energy transfer can be excluded by the reaction quenching experiment using naphthalene. As shown later, the quantum yield of the isomerization is considerably reduced by the presence of naphthalene: at 2 M of naphthalene, 57% quenching for **1c**→**2c**; 29% quenching for **2c**→**1c**. At the same concentration of naphthalene, however, the fluorescence of anthryl groups is not quenched at all, though the fluorescence is slightly red-shifted (ca. 1 nm). These results suggest the energy transfer from the upper excited states of anthryl groups; most plausibly via the T_2 states.

Liu and co-workers have demonstrated that T_2 state of substituted anthracenes can sensitize some photoreactions.[3] They estimated the lifetime of the T_2 state of 9,10-dibromoanthracene to be ca. 20 ps. Therefore, it may be reasonable to assume that the T_2 state of anthryl groups of **1c** and **2c** is the reactive excited state for the isomerization. If the presumption of the intramolecular T_2 sensitization is accepted, the observed diastereoselectivity is explained in a similar manner with our previous study as *follows*: the rate of energy transfer from the T_2 state of anthryl to the fluorenyl moiety is slower in **1c** (see **A** and **B**) because of the steric repulsion between the methyl and the fluorenyl group.[1]

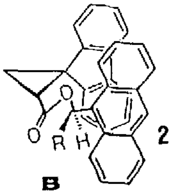
To test the possibility of selective energy transfer from the T_2 state of anthryl groups, the intensities of T-T absorption of **1c** and **2c** were measured. As shown in Figure 1, the intensity of T-T absorption of **1c** is higher than that of **2c**. The difference of the intensities shows the difference of the concentration of the T_1 states, provided that the molecular extinction coefficients of T_1 states of anthryl groups of **1c** and **2c** are nearly equal. The higher production of T_1 state of **1c** is in accordance with the slower rate of the intramolecular energy transfer, giving higher yield of T_1 state via a rapid internal conversion process in **1c**.

A much clear evidence was provided by the Stern-Volmer quenching experiment (naphthalene as a quencher), which allows the estimation of the lifetimes of reactive states. Since the singlet (92 kcal/mol) and triplet energies (61 kcal/mol) of naphthalene are well higher than those of anthracene (E_{S1}=76; E_{T1} = 42 kcal/mol) respectively, the S_1(anthryl)→S_1 (naphthalene) and T_1→T_1 energy transfers are highly endothermic.2) However, the energy transfer from the T_2 state of the anthryl groups (anthracene: E_{T2}=74.4



1c

A



2c

B

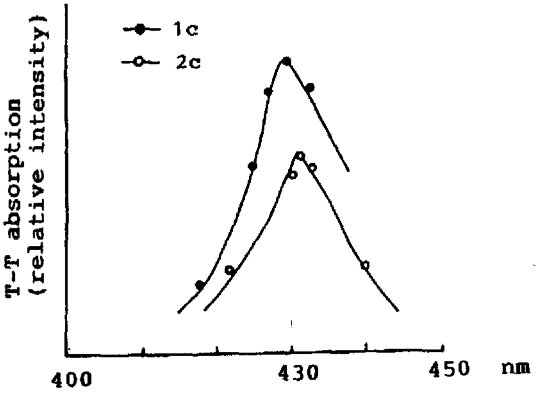


Figure 1. T-T absorption spectra of anthryl groups of **1c** and **2c** obtained by flash photolysis experiments at 40 μs after flash at 20°C in benzene under argon: [**1c**] = [**2c**] = 1.2 x 10^{-3} M.

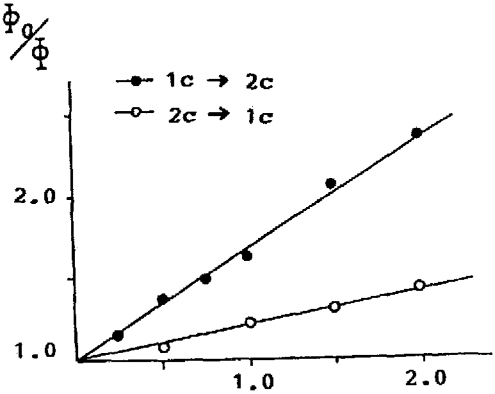


Figure 2. Stern-Volmer plot for the isomerization (**1c**⇄ **2c**) by naphthalene in benzene at room temperature.

kcal/mol)[3] to naphthalene (T_1) is an exothermic process. For this reason, naphthalene would quench only the T_2 state of the anthryl group. Figure 2 shows the Stern-Volmer plot for the isomerization. Assuming the diffusion controlled rate constant (1.6×10^{10} $M^{-1}s^{-1}$)[2,3] for the T_2 quenching, the lifetimes of the anthryl groups are estimated to be 42 ps for **1c**, and 13 ps for **2c**. These values are compatible with the models of **A** and **B** which predict the faster intramolecular energy transfer in **2c**. Furthermore, the fact that the order of the T_2 lifetimes is same with that obtained by Liu et al.[3] strongly indicates that the reactive excited state is the T_2 state of the anthryl groups.

Although we have thus succeeded to obtain evidences for the selective energy transfer from the T_2 state, the difference between the T_2 lifetimes of anthryl groups of **1c** and **2c** is only about 3 times. This small difference would be probably ascribed to the fast internal conversion process which competes with the intramolecular energy transfer. Therefore, the observed difference of the T_2 lifetimes may not well reflect the difference of the rate of energy transfer.

As can be expected from the above experiments, asymmetric synthesis is easily achieved when the chiral α-(9''-anthryl)ethyl group is introduced. Thus, similar irradiation of an equimolar mixture of **1c** and **2c**, prepared using optically pure R-(+)-α-(9-anthryl)ethanol,[4] produced, after hydrolysis and diazomethane treatment, the optical active methyl (2S)-(+)-spiro[cyclopropane-1,9'-fluorene]-2-carboxylate[5] in 91% optical yield (94% chemical yield), $[\alpha]_D = +242°$(c = 0.3, EtOH).

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