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REDOX-PHOTOSENSITIZED STEREOMUTATION OF 1-PHENOXYPROPENE; CATALYSIS BY THE CATION RADICAL OF AROMATIC HYDROCARBONS[1)]

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The stereomutaion of 1-phenoxypropene occurred by the redox-photosensitization using aromatic hydrocarbon-dicyanobenzene-acetonitrile systems, giving rise to a photostationary mixture of the cis- and trans-isomers in 1:1-ratio. The combined quantum yields for the trans→cis and cis→trans isomerizations were over unity. The mechanism is discussed in terms of catalysis by the cation radical of aromatic hydrocarbons.

Numerous studies have been done on cis,trans-isomerism of olefins in either the ground state[2)] or the electronically excited states.[3)] However, only a few papers on stereomutations of olefins via the ion radicals have been published so far. Recently, radiation-induced isomerization of cis-2-butene is reported to occur via the cation radical by means of a chain reaction mechanism,[4)] while the trans-isomer does not isomerize. Likewise, cis-stilbene efficiently isomerizes to the trans-isomer upon γ-radiation of benzene solution;[5)] a chain mechanism involving the anion radical is suggested. We wish to report here the redox-photosensitized stereomutation of 1-phenoxypropene, using aromatic hydrocarbon-p-dicyanobenzene-acetonitrile systems.[6)]

Irradiation of an acetonitrile solution containing an aromatic hydrocarbon (S), p-dicyanobenzene (DCNB), and cis- or trans-1-phenoxypropene (c-P or t-P) at 313 nm resulted in loss of stereointegrity of the starting olefin, ultimately giving rise to a photostationary mixture of c-P and t-P in 1:1-ratio (Figure 1).

At a photostationary state, the material balance was over 95%. Further irradiation of a photostationary mixture led to a slow consumption of the olefins, forming other products which appear to be dimers of the olefin, whereas S and DCNB were completely recovered. When benzene or ethyl acetate was used as solvent, the photoisomerization did not occur at all. The coexistence of S and DCNB was found to be essential for the photosensitized isomerization. Notably, quantum yields for the cis,trans-isomerization (Table 1) increase with an increase in oxidation potentials of S.

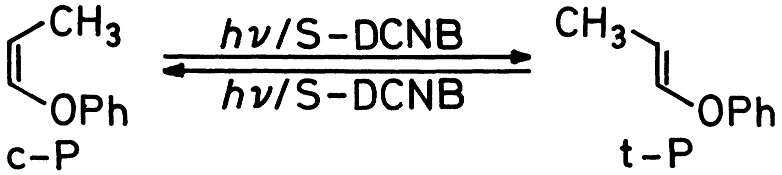


Table 1. Quantum Yields for cis,trans-Isomerization of c-P and t-P[a)]

S ($E_{1/2}^{ox}$, V)[b)]		$\Phi_{c\rightarrow t}$	$\Phi_{t\rightarrow c}$
Pyrene	(0.78)	~0.0	~0.0
Chrysene	(1.05)	0.58	0.33
Phenanthrene	(1.17)	0.66 (0.95)[c)]	0.41 (0.58)[c)]
Naphthalene	(1.20)	0.74	0.54
Triphenylene	(1.29)	0.81 (1.19)[c)]	0.58 (0.81)[c)]

a) [S] = 1×10^{-2} M, [DCNB] = 1×10^{-1} M, and [c-P or t-P] = 1×10^{-4} M in acetonitrile; irradiation at 313 nm. b) Half-wave values of oxidation potentials vs. Ag/Ag$^+$ determined by cyclic voltammetry. $E_{1/2}^{ox}$ of c-P and t-P = 1.38 V. c) Limited quantum yields ($\Phi^{\infty}_{c\rightarrow t \text{ or } t\rightarrow c}$) extraporated to infinite concentration of c-P and t-P.

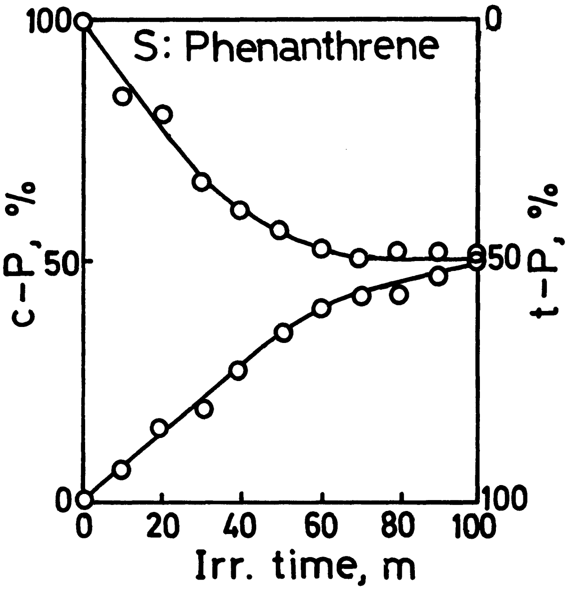
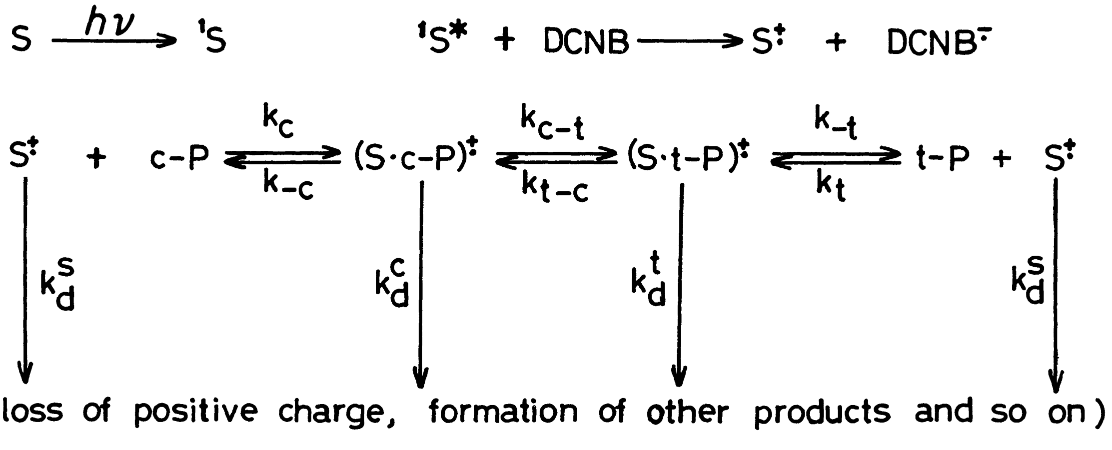


Figure 1. Plots of c-P or t-P % vs. irradiation time; [S] = 1×10^{-2} M, [DCNB] = 1×10^{-1} M, and [c-P or t-P] = 1×10^{-4} M; at 313 nm.

Triplet mechanisms for the photosensitized isomerization can be safely excluded, since 1.0 M of isoprene did not quench the isomerization at all. UV spectra revealed that charge-transfer complexes are not formed in the ground state. Moreover, the fluorescence of S was not quenched by c-P and t-P at all. Thus, the olefins do not interact with S in either the ground or excited singlet state and with DCNB in the ground state.

As stated earlier,6) electron transfer from excited singlet S ($^1S^*$) to DCNB is responsible for the initiation process,6a) being in accord with the requirements for the occurrence of the photosensitized isomerization that aprotic polar solvent and the coexistence of S and DCNB are essential. For mechanistic elucidation, it should be noted that the values of $\Phi^{\infty}_{c\to t}$ plus $\Phi^{\infty}_{t\to c}$ are over unity,7) and that quantum yields depend on oxidation potentials of S. This suggests that the isomerization proceeds by means of a chain reaction mechanism involving the cation radical of S ($S^{\overset{+}{\cdot}}$). However, the oxidation potentials of S are considerably lower than those of c-P and t-P. Therefore, it is suggested that the cation radical of S forms π-complexes with the olefins6) which act as key intermediates; partial development of the positive charge on the olefin side would lead to a decrease in bond order of the olefinic double bond, thus making the double bond capable of bond rotation. Simplified reaction pathways are shown below. Chain termination processes would involve loss of the positive charge of cation radicals, formation of other products and so on.



At the photostationary state, $[c\text{-}P]/[t\text{-}P] \simeq (k_t/k_{-t})\times(k_{-c}/k_c)\times(k_{t-c}/k_{c-t}) = K_t/(K_c\cdot K_{c-t}) = 1.0$, provided $k_{-c} \gg k_d^c + k_{c-t}$, $k_{-t} \gg k_d^t + k_{t-c}$, and $k_c[c\text{-}P]$ or $k_t[t\text{-}P] \gg k_d^S$. If $k_d^c \simeq k_d^t$, $\Phi^{\infty}_{c-t}/\Phi^{\infty}_{t-c} \simeq k_{c-t}/k_{t-c} = K_{c-t} = 1.5$ (S = triphenylene) or 1.65 (S = phenanthrene), from which K_t/K_c can be calculated to be 1.5 or 1.65. These values suggest that the isomerization of $(S\cdot c\text{-}P)^{\overset{+}{\cdot}}$ to $(S\cdot t\text{-}P)^{\overset{+}{\cdot}}$ slightly predominates over the reverse reaction, whereas formation of $(S\cdot c\text{-}P)^{\overset{+}{\cdot}}$ from $S^{\overset{+}{\cdot}}$ and c-P is correspondingly less favorable than that of $(S\cdot t\text{-}P)^{\overset{+}{\cdot}}$ from $S^{\overset{+}{\cdot}}$ and t-P.

Alternatively, the complete hole transfer from $S^{\dot{+}}$ to c-P or t-P would occur to form $c\text{-}P^{\dot{+}}$ or $t\text{-}P^{\dot{+}}$, which would lose stereointegrity. Electron transfer from S to $c\text{-}P^{\dot{+}}$ and $t\text{-}P^{\dot{+}}$ would regenerate $S^{\dot{+}}$ along with the stereomutation of the olefin. However, this mechanism appears to be unfavorable since the hole transfer process is considerably endothermic. In this regard, we are now intending to investigate radiation-induced stereomutation of c-P and t-P.

Finally, it should be noted that the redox-photosensitized isomerization of trans-β-methylstyrene and trans-anethole was found to occur in either the absence or the presence of isoprene, giving again photostationary mixtures of the cis- and trans-isomers in 1:1-ratio. The redox-photosensitization would thus provide another route for stereomutations of olefins.

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References and Footnote

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7) The values do not necessarily indicate the true chain lengths, since quantum yields of reactive cation radicals of S are probably less than unity.

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