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"ONE-WAY" PHOTOISOMERIZATION BETWEEN CIS- AND TRANS-OLEFIN. A NOVEL ADIABATIC PROCESS IN THE EXCITED STATE

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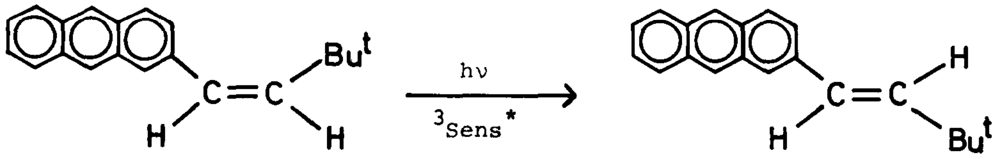
Summary: Triplet sensitized and unsensitized irradiation of 1-(2-anthryl)-3,3-dimethyl-1-butene in benzene resulted in "one-way" isomerization from the cis- to trans-isomer giving almost 100% of the trans-isomer through a quantum chain process. No "return" isomerization from the trans- to cis-isomer occurred. The isomerization can be interpreted in terms of an adiabatic process in the triplet excited state.

Photochemical cis-trans isomerization of olefins has extensively been investigated.[1-5] Acyclic olefins generally give a mixture of the cis- and trans-isomer at the photostationary state irrespective of direct or sensitized irradiation.[1] Concerning isomerization through the triplet manifold, it is generally accepted that the planar transoid ($^3t^*$) and cisoid ($^3c^*$) triplets undergo relaxation into the twisted triplet ($^3p^*$), which subsequently undergoes diabatic transition to the twisted ground state (p^0) followed by its deactivation to a mixture of the cis (c^0) and trans isomer (t^0) with a certain partition ratio (Figure 1).[1]

Recently, we have found that a new series of aromatic olefins carrying a large aromatic group on one of the ethylenic carbons and an alkyl group on the other like 1-(2-naphthyl)-3,3-dimethyl-1-butene (2-NpCH=CHBu^t, DMNB) exhibit characteristic properties of the triplet state[6-8] different from stilbene[1] and β-alkylstyrenes;[9,10] $^3t^*$ is equilibrated with $^3p^*$ and has a population as high as $^3p^*$.[6-8] On the basis of these findings we have proposed a classification of energy surfaces of the triplet states of aromatic olefins by the energy difference between $^3t^*$ and $^3p^*$.[7]

In the course of extending the investigation on the new series of aromatic olefins, we found that the cis-isomer of 1-(2-anthryl)-3,3-dimethyl-1-butene (ADMB) gave in a "one way" fashion almost 100% of the trans-isomer on triplet



cis-ADMB trans-ADMB

sensitization, and that no "return" isomerization from the trans isomer occurred. This finding makes a remarkable contrast with the well known photoisomerization of acyclic olefins.[11]

In a typical run, cis-ADMB (0.003 mol dm^{-3}) was irradiated in benzene (3 ml) in the presence of Michler's ketone (0.005 mol dm^{-3}) as a triplet sensitizer with 313-nm light obtained through an aqueous potassium chromate filter[13] and a Toshiba UV-D33S glass filter from a 400 W high pressure mercury lamp. The isomerization was almost complete within a few minute as determined by GLPC. However, irradiation of trans-ADMB in place of the cis-isomer under otherwise the same conditions did not give any detectable amount of the cis isomer even on prolonged irradiation for more than one hour.

Also remarkable is the initial quantum yield for the cis-to-trans isomerization exceeding unity; $\Phi_{c\rightarrow t}$ = 4.2 in benzene. These remarkable facts indicate that the energy surface of the excited triplet state of the present olefin must be highly different from those of the usual olefins.[1]

A similar one-way isomerization of ADMB was observed on direct irradiation with 313-nm light in benzene; $\Phi_{c\rightarrow t}= 2.3$, $\Phi_{t\rightarrow c} = 0$.

Since the triplet energies of the cis- and trans-ADMB[14] are estimated to be as low as or less than that of anthracene, 42 kcal mol^{-1},[13] triplet Michler's ketone (E_T = 62 kcal mol^{-1})[13] will undergo effective energy transfer to both isomers. If the isomerization would proceed through the decay of $^3p^*$ to the ground state, the isomer ratio at the photostationary state ($[cis]/[trans]_{pss}$) should take a non-zero value. However, this is not the case for the present olefin. Accordingly, the present result clearly indicates that the generally accepted mechanism[1] does not hold for ADMB.

On taking account that $^3t^*$ of DMNB, a naphthyl analogue of ADMB, is fairly stabilized and almost in the same energy level as $^3p^*$,[7,8] it is highly probable that the minimum is located at $^3t^*$ but not at $^3p^*$ in the triplet energy surface of ADMB and that $^3t^*$ is the sole funnel crossing to the ground state; $^3t^*$ decays to the trans-isomer as depicted in Fig. 2.

The large quantum yield on the triplet sensitization clearly shows that the isomerization proceeds through a quantum chain process,[6,15] where the decay of the excited triplet to the trans-isomer involves formation of any excited species bringing about isomerization of the cis isomer. Energy transfer from $^3t^*$ to the cis-isomer must be the only possible process to regenerate $^3c^*$. Other possible mechanisms to constitute the quantum chain process are eliminated. Thus, the back energy transfer from $^3t^*$ to Michler's ketone to regenerate the sensitizer triplet could not occur, since the triplet energy of trans-ADMB is estimated to be nearly 20 kcal mol^{-1} lower than that of the sensitizer. Another possibility is excluded that the minimum would occur at $^3p^*$ in the lowest triplet surface of ADMB but it would be rather shifted to the side of the trans conformation, and thus deactivation of $^3p^*$ would give exclusively the trans-isomer, since the energy evolved in this transition would be much less than the triplet energy of the cis-isomer. Therefore, the mechanism for the triplet sensitized cis-to-trans isomerization of ADMB can be expressed by Scheme 1.

It is noticeable that the present isomerization proceeds through a novel adiabatic process along the triplet energy surface, contrasting with most photochemical reactions which are known to take place through diabatic processes.[16] This unique process might arise from the presence of an anthryl group, the very low triplet energy of which plays an important role in stabilizing $^3t^*$ on the lowest triplet surface.

The unsensitized irradiation of ADMB also shows similar trends to the triplet sensitization as mentioned above. At present we assume that this isomerization proceeds on the triplet manifold.[17]

Finally, it should be noted that the present "one-way" isomerization of the olefin will certainly open a new gate for elucidation of the nature of the adiabatic processes in the excited states.

Scheme 1

$$^3s^* + c^0 \longrightarrow s^0 + {}^3c^* \qquad (1)$$

$$^3c^* \longrightarrow {}^3p^* \longrightarrow {}^3t^* \qquad (2)$$

$$^3t^* + c^0 \longrightarrow t^0 + {}^3c^* \qquad (3)$$

$$^3t^* \longrightarrow t^0 \qquad (4)$$

$$^3p^* \not\longrightarrow p^0 \longrightarrow \alpha t^0 + (1-\alpha)c^0 \qquad (5)$$

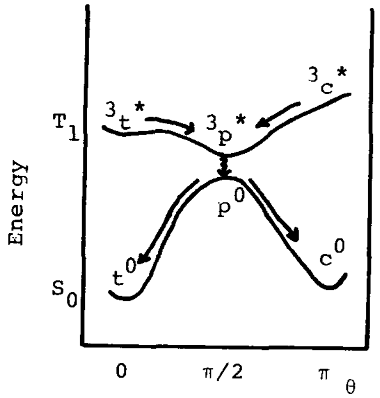


Figure 1. The general mechanism of cis-trans isomerization of aromatic olefins; θ denotes the angle of twist around the ethylenic linkage

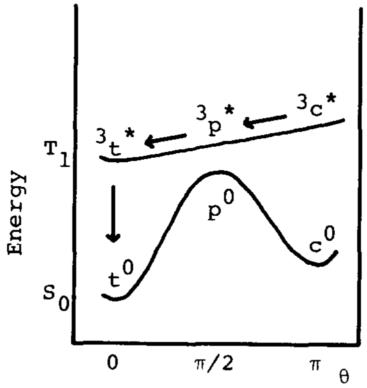


Figure 2. A possible mechanism for adiabatic isomerization of ADMB; θ denotes the angle of twist around the ethylenic linkage

References

1) J. Saltiel and J. L. Charlton, "Rearrangements in Ground and Excited states," Vol. 3, P. de Mayo, Ed., Academic Press, New York, 1980, p 25, and references therein.

2) K. Tokumaru and T. Arai, Kagaku, 1982, 37, 235.

3) H. Görner and D. Schulte-Frohlinde, Ber. Bunsenges. Phys. Chem., 1979, 81, 713.

4) M. Sumitani, N. Nakashima, and K. Yoshihara, Chem. Phys. Lett., 1979, 68, 255.

5) T. Wismonski-Knittel and E. Fischer, J. Chem. Soc. Perkin II, 1979, 449.

6) T. Arai, H. Sakuragi, and K. Tokumaru, Chem. Lett., 1980, 1335.

7) T. Arai, T. Karatsu, H. Sakuragi, and K. Tokumaru, Chem. Lett., 1981, 1377; J. Photochem., 1981, 17, 107.

8) T. Arai, H. Sakuragi, K. Tokumaru, Y. Sakaguchi, J. Nakamura, and H. Hayashi, Chem. Phys. Lett., 1983, in press.

9) T. Arai, H. Sakuragi, and K. Tokumaru, Chem. Lett., 1980, 261; Bull. Chem. Soc. Jpn., 1982, 55, 2204.

10) R. E. Schwerzel and R. A. Caldwell, J. Am. Chem. Soc., 1973, 95, 1382.

11) Photoisomerizations of diarylethylenes such as 1,2-bis(9-anthryl)ethylene[12] and 1,2-bis(3-phenanthryl)ethylene[5] were reported to be inefficient because of their steric and other effects.

12) H. D. Becker, K. Sandor, and L. Hansen, J. Org. Chem., 1981, 46, 821; H. D. Becker, L. Hansen, and K. Anderson, ibid, 46, 5419.

13) S. L. Murov, "Handbook of Photochemistry," Marcel Dekker, New York, 1973.

14) Since ADMB has a larger π conjugation system than anthracene, the triplet excitation energy of ADMB should be smaller than that of anthracene.

15) J. A. Marcel-Smith and D. G. Whitten, J. Am. Chem. Soc., 1978, 100, 2620.

16) N. J. Turro, J. Mcvey, V. Ramamurthy, and P. Lechtken, Angew. Chem. Internat. Ed. Engl., 1979, 18, 572; G. Jones II, and S.-H. Chiang, J. Am. Chem. Soc., 1979, 101, 7421.

17) Fluorescence lifetime and fluorescence quantum yields were determined to be 6.5 and 10.4 ns, and 0.43 and 0.52 for the cis- and trans-isomer, respectively. If the isomerization took place through the singlet manifold, the excited trans singlet should regenerate the excited cis singlet through energy transfer with a rate constant of no more than 10^9 dm^3 mol^{-1} s^{-1}. This requires that the excited trans singlet should be alive no less than 10^{-6} s, which contrasts with the measured lifetime of 10.4 ns.

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