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PHOTOCHEMICAL GEOMETRICAL ISOMERIZATION OF A C=C-C=N SYSTEM. BEHAVIOR OF THE FOUR STEREOISOMERS OF 1-METHOXYIMINO-3-PHENYL-2-PROPENE

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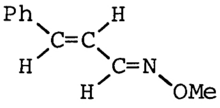
Irradiation of the four isomers, trans-anti, trans-syn, cis-anti, and cis-syn, of 1-methoxyimino-3-phenyl-2-propene, a conjugated imine, resulted in cis-trans, syn-anti, and concurrent cis-trans and syn-anti isomerization. The photostationary isomer ratio and the quantum yields of the isomerization from each isomer were determined to elucidate the mechanism of the isomerization.

Currently active effort has been done to elucidate the mechanism of vision, and the initial photochemical processes taking place through cis-trans isomerization of retinal and its model compounds have precisely been investigated.1) However, photochemical behavior of simpler conjugated imines, which are of great importance as a model for higher homologues, has not yet been clarified probably because of difficulty in obtaining pure geometrical isomers. In N-alkyl- and N-aryl-imines the energy barriers between their syn and anti isomers are generally too low to allow pure isolation at room temperature.2) Accordingly, for the simpler conjugated imines, it has not been clear even which of their carbon-carbon and carbon-nitrogen double bonds preferentially undergoes the geometrical isomerization upon irradiation3) in contrast with the isomerization of conjugated dienes and trienes investigated precisely.4,5)

We have attempted to clarify this aspect by employing 1-methoxyimino-3-phenyl-2-propene (I), the four stereoisomers of which, trans-anti (ta), trans-syn (ts), cis-anti (ca), and cis-syn (cs) isomers, are now found to be thermally so stable that their mutual photoisomerization can be examined by gas chromatographic analysis. This paper reports the photochemical behavior of these four isomers to show that cis-trans, syn-anti, and even concurrent cis-trans and syn-anti isomerizations take place with different efficiencies depending upon the isomers.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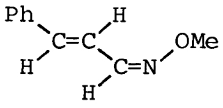
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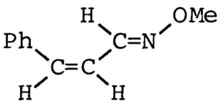
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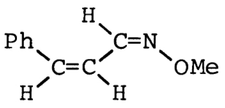

cs

In preparation of I, trans-3-phenylpropenal was refluxed in aqueous ethanol with methoxyamine hydrochloride and sodium acetate to give a mixture of the ta and ts isomers. Irradiation of this mixture in methanol with a high pressure mercury lamp afforded a mixture of all of the four isomers. The ta, ts, and ca isomers were separated by column chromatography over silica gel, and the cs isomer was isolated by preparative GLPC. The four isomers obtained were satisfactorily pure by GLPC and their configurations were reasonably assigned on the basis of UV and NMR data.6)

On irradiation of the isomers (4.5×10^{-3} mol/dm^3) for 60 h in degassed benzene solutions (3 ml) with 313-nm light isolated from a 400 W high pressure mercury lamp through an aqueous potassium chromate solution,7) each isomer afforded a photostationary mixture of the same composition of the four isomers as follows;

ta, ts, ca, cs: 37, 31, 6, 26%

The quantum yields for the initial stages of isomerization were determined for each isomer (4.5×10^{-3} mol/dm^3) at conversion as low as 5-13% in benzene (3 ml) under argon atmosphere on irradiation with 313-nm light. The results are schematically summarized in Scheme 1, where the figures on each arrow represent the quantum yields for the corresponding processes; the bold, solid, and dotted arrows denote the processes with high ($\geq$0.1), medium (0.01-0.1), and low ($\leq$0.01) quantum yields, respectively.

The results shown in Scheme 1 indicate the following characteristic features of the photoisomerization of I;

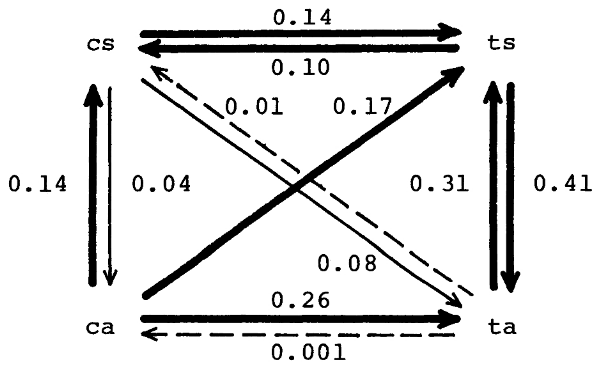
1) As to the cis-trans isomerization, each cis isomer tends to isomerize into the trans isomers with as well as without change of the configuration around the carbon-nitrogen double bond. However, the reverse isomerization from the trans to cis isomers does not proceed so efficiently as the cis→trans isomerization; particularly ta is highly reluctant to the trans→cis isomerization and ts isomerizes into the cis form exclusively retaining the C=N configuration.

2) The syn-anti isomerization takes place from each isomer with quantum yields varying widely with the isomers. Both trans isomers particularly undergo most efficiently the syn-anti isomerization retaining the C=C configuration among their isomerization processes; however, their syn-anti isomerization accompanied by the trans→cis isomerization is not efficient, and ts never isomerizes into ca. Both cis isomers undergo the syn-anti isomerization; the isomerization accompanied by the cis→trans isomerization is slightly more efficient than that without the latter. The ca isomer undergoes the anti→syn isomerization into ts and cs; however, cs undergoes the syn→anti isomerization less efficiently than does ca.

3) As mentioned in 1) and 2), it is very noticeable that the cis isomers do undergo the concurrent cis-trans and syn-anti isomerization along with the single isomerization around the C=C or C=N bond. The concurrent isomerization is not the result of stepwise isomerizations; for example, ca does not isomerize through a process like ca→ta→ts or ca→cs→ts. The quantum yields were determined only in the initial stage of the reaction, and accordingly, the concentrations of the singly isomerized compounds were very low to absorb enough light quanta for the efficient stepwise isomerizations.8)

The tentative energy surface of the excited state is depicted in Fig. 1 on the basis of the above results and by taking account of the energy difference

Scheme 1.



between the cis and trans isomers in their ground and excited states.9,10) In the ground state, the cis isomers must be higher in energy than the trans isomers due to the steric repulsion between the phenyl and N-methoxyimino groups as seen from the lower molar extinction coefficients of the cis isomers than those of the trans isomers in their absorption spectra.6) Since the excitation energies for the cis isomers are only slightly higher than those for the trans isomers, the excited cis isomers are estimated to be higher in energy than the excited trans isomers by nearly the same energy difference in the ground state.6,11)

All isomerizations do not proceed through a single common intermediate, since, for example, the ratio of quantum yields for the production of ca and cs are very much different between the isomerizations starting from ts and from ta. Among the isomers, ca isomerizes most facilely into the other three isomers probably due to low energy barriers; however, cs does not so efficiently isomerize as ca. These facts suggest two possible profiles for the energy surfaces. First, the excited cs might be surrounded by higher energy barriers for the isomerization than the excited ca; however, the excited ta must be situated in the lowest energy among the isomers because ta isomerizes only in low efficiency except into ts. Alternatively, the excited states twisted around the C=C and C=N bonds might deactivate to favorable points of the ground state surface to attain cs. However, the results cannot be explained only by the latter mechanism, since the sum of the quantum yields for isomerization to cs from the other isomers, 0.25, is far lower than the quantum yield for decaying to the starting cs, 0.74.

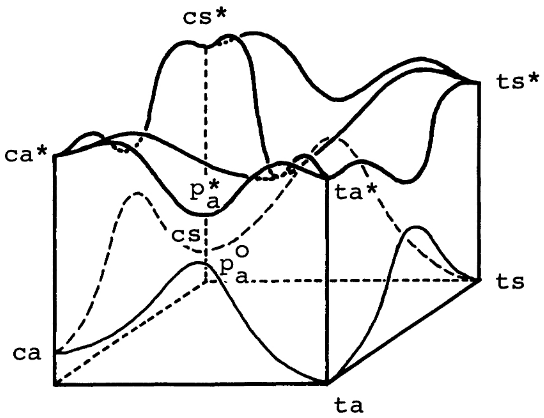


Fig. 1. Schematic surface description of the isomerization of I.

Finally, it should be noted that the present results on the efficiency for the different modes of isomerization of the simple conjugated imine will contribute to understanding photochemistry of more complicated compounds of biological importance.

References

1) For example, K. Nakanishi, Pure Appl. Chem., 49, 333 (1977); Also see, Acc. Chem. Res., 8 (1975), March issue.

2) H. Ohta and K. Tokumaru, Yuki Gosei Kagaku Kyokaishi, 30, 1006 (1972); A. Padwa, Chem. Rev., 77, 37 (1977).

3) T. Sato, T. Inoue, and K. Yamamoto, Bull. Chem. Soc. Jpn., 45, 1176 (1972).

4) Y. C. C. Butt, A. K. Singh, H. B. Baretz, and R. S. H. Liu, J. Phys. Chem., 85, 2091 (1981).

5) Photochemical geometrical isomerization of the carbon-nitrogen double bond of an imine was reported by Padwa et al. (A. Padwa and F. Albrecht, J. Am. Chem. Soc., 96, 4849 (1974).)

6) The absorption maximums of the four isomers are as follows: λ_{max}/nm (ε): ta, 289 (30 000); ts, 289 (27 500); ca, 280 (20 000); cs, 280 (19 500). Other spectroscopic properties will be reported elsewhere.

7) S. L. Murov, "Handbook of Photochemistry," Marcel Dekker, New York (1973), p. 97.

8) For example, for the ca→ts isomerization, if 10% of the starting isomer isomerizes singly at the C=C or C=N double bond, the quantum yields (Φ) of the stepwise processes, ca→ta→ts and ca→cs→ts, are given by using the molar extinction coefficients (ε) at 313 nm as follows:

$$\Phi_{ca\rightarrow ts} = \Phi_{ca\rightarrow ta}[0.1\varepsilon_{ta}/(0.9\varepsilon_{ca} + 0.1\varepsilon_{ta})]\Phi_{ta\rightarrow ts} \cong 0.024$$
$$\Phi_{ca\rightarrow ts} = \Phi_{ca\rightarrow cs}[0.1\varepsilon_{cs}/(0.9\varepsilon_{ca} + 0.1\varepsilon_{cs})]\Phi_{cs\rightarrow ts} \cong 0.003$$

These values are less than the quantum yield obtained for the ca→ts isomerization, 0.17. The situation is the same for the cs→ta isomerization. (ε at 313 nm: 15 200, 16 900, 3 900, and 5 500 for ta, ts, ca, and cs, respectively.)

9) On direct irradiation, the isomerization seems to take place from the singlet manifold, since the triplet sensitization gives a completely different photostationary isomer ratio. (A. Okami, T. Arai, H. Sakuragi, and K. Tokumaru, Presented at the 47th Annual Meeting of the Chemical Society of Japan, Kyoto, April 1983, Abstracts II, p. 762.)

10) In Fig. 1, the axes perpendicular to the energy axis mean the reaction coordinates as a function of the C-C and C-N rotations. The isomerization from ca to ta, for example, takes place through the processes, $\text{ca} + h\nu \longrightarrow \text{ca}^* \longrightarrow p_a^* \longrightarrow p_a^o \longrightarrow \alpha\text{ca} + (1-\alpha)\text{ta}$. However, in the isomerization around the C=N double bond the two modes, rotation and inversion, might be possible.

11) Each isomer was found to be non-emissive at 77 K.

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