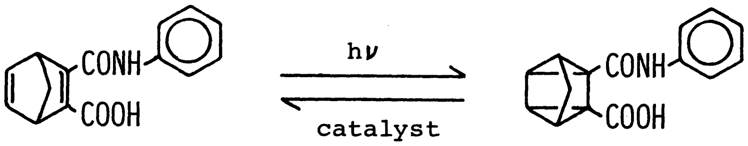
CHEMISTRY LETTERS, pp. 1699-1702, 1982.

A WATER-SOLUBLE SOLAR ENERGY STORAGE SYSTEM

Kazuhiro MARUYAMA* and Hitoshi TAMIAKI
Department of Chemistry, Faculty of Science,
Kyoto University, Kyoto 606

In an alkaline aqueous solution, photochemical valence isomerization of norbornadiene derivative 1 to quadricyclane derivative 2 occurred quantitatively, and reverse isomerization of 2 to 1 under release of heat was achieved by catalytic action of cobalt hematoporphyrin 3 and analogues. This system may be of a great practical use for a solar energy storage.

It is an urgent problem to pack solar energy into a form available at a desirable time. Valence isomerization of organic compounds induced by solar radiation will provide a promising key for the solution. On irradiation by sunligth some organic compounds may be converted to the stable but energy rich isomers which under treatment with suitable catalyst release heat to return to the original forms. Valence isomerization between norbornadiene and quadricyclane has attracted much attentions from the above point of views.[1-3)] All of the systems invesigated so far, however, have used organic solvents as the reacting media, and then have a great disadvantage for the actual use because of their inflammability and high cost. In this report, a water-soluble solar energy storage system, safe and less expensive, is described.



1 2

Fig. 1 Water-soluble solar energy storage system

We synthesized norbornadiene derivative 1 having both of carboxyl and amide groups.[4)] The compound 1 was highly soluble in an alkaline solution and was stable in a boiling aqueous sodium carbonate solution. The absorption band of 1 shifted to longer wavelength than that of norbornadiene. This made 1 absorb sunlight. When 1 was irradiated in open air in an aqueous sodium carbonate solution with sunlight (or light of the wavelength 300-400 nm), the corresponding quadricyclane derivative 2 was quantitatively formed. The photoisomerization was so clean that a sharp isosbestic point appeared in the spectral change as shown in Fig. 2. Such a sharp isosbestic point was attainable in the pH range from about 7 to 14. The quantum yield from 1 to 2 at 366 nm was 0.02 without expelling of air. For example, $1\text{x}10^{-4}$M of 1 in an aqueous sodium carbonate solution was completely converted to 2 within 0.5 hour on clear daylight radiation (in Kyoto, 1982 July 15, 1:30-2 pm).

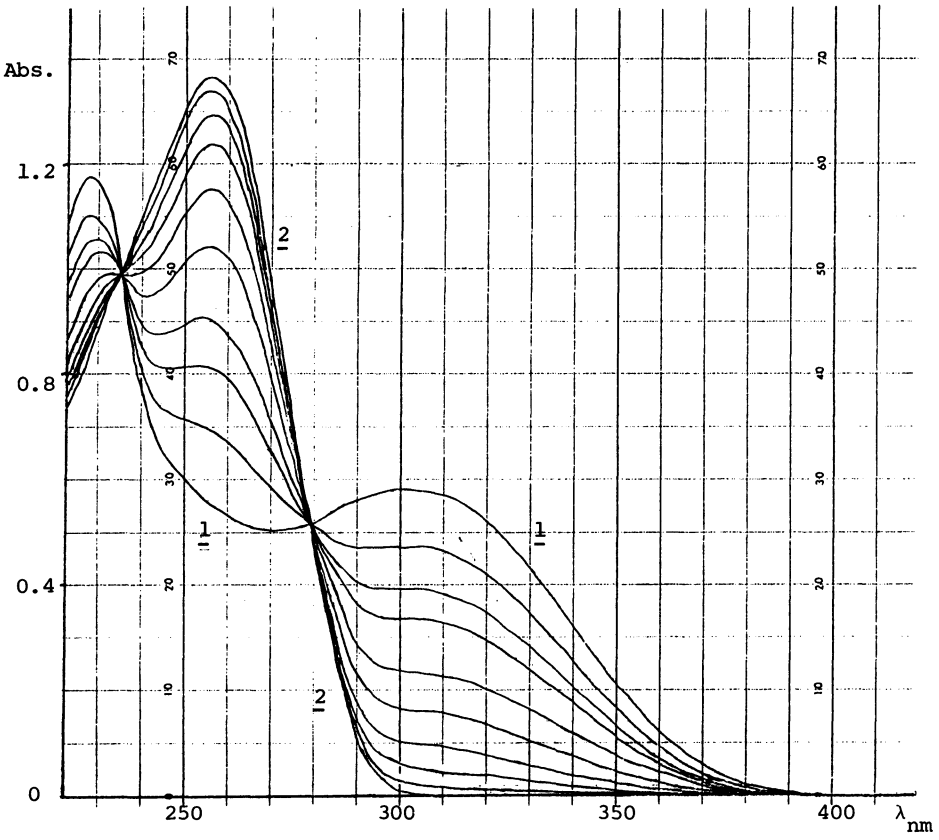
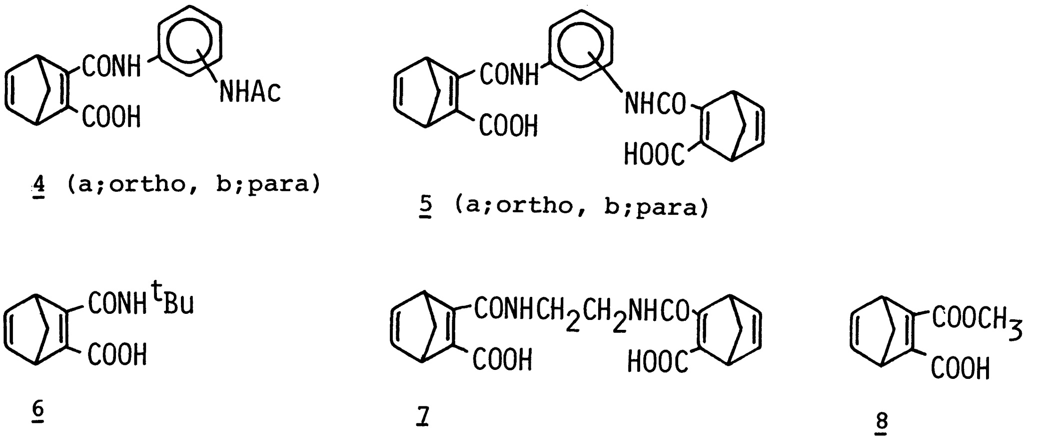


Fig. 2 UV spectra of the photoisomerization of 1 to 2. $1\text{x}10^{-4}$M of 1 in $1\text{x}10^{-2}$M Na_2CO_3 aq. was irradiated with sunlight.



4 (a;ortho, b;para)

5 (a;ortho, b;para)

6

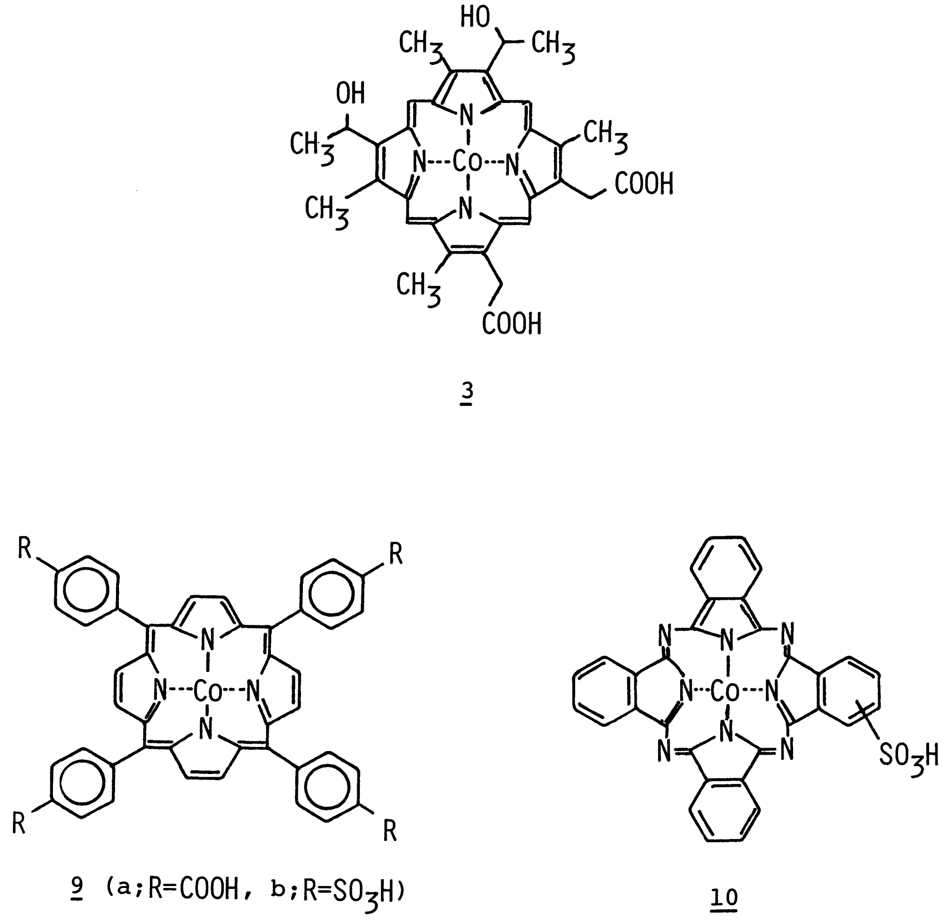
7

8

Fig. 3 Norbornadiene derivatives

The isomerized 2 was so stable in a boiling aqueous sodium carbonate solution that none of 1 and other products could be produced under the conditions. Surprisingly, however, addition of a catalytic amount of cobalt hematoporphyrin 3 in the solution at room temperature induced a sudden isomerization of 2 to 1 quantitatively under release of heat. The heat of isomerization was about 60 kJ mol^{-1}. The photoisomerization and catalytic back process were completely reversible even in the presence of air. The pseudo-first order rate constant of the back isomerization was 2 $M^{-1}s^{-1}$ at 25°C, and for example, the half life of 2 was 6 min at 25°C ($[2]/[3]=4x10^{-1}M/8x10^{-4}M=1/0.002$).

The analogues of 1, 4a, 4b, 5a, 5b, 6, 7, 8, showed similar photochemical behavior and releasing heat went back to the original forms under action of 3. Water-soluble cobalt porphyrin and phthalocyanine derivative 9a, 9b, 10 (dye; C.I. 74140), were similarly applicable as the catalysts. Iron porphyrins (hemin), cobalt corrinoids (vitamin B_{12}) and cobaloximes (bis(dimethylglyoximato)cobalt complexes) had also catalytic activity. Since water-soluble cobalt porphyrin and phthalocyanine derivatives bound with polymer may act as the catalyst, our water-soluble solar energy storage system would be of a great actual use.



3

9 (a;R=COOH, b;R=SO_3H)

10

Fig. 4 Catalysts

References

1) T.Laird, Chem.Ind.(London), 1978, 186.

2) G.Jones.II , S.Chiang and P.T.Xuan, J.Photochem., 10, 1 (1979).

3) R.R.Hautala, R.B.King and C.Kutal, "Solar Energy; Chemical Conversion and Storage" The Humana Press 1979.

4) K.Maruyama, K.Terada and Y.Yamamoto, J.Org.Chem., 46, 5294 (1981).

(Received August 13, 1982)