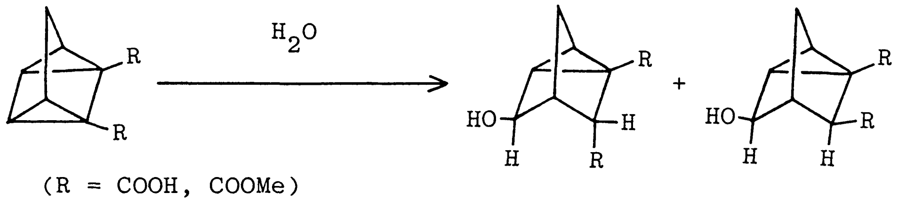
CHEMISTRY LETTERS, pp. 1875-1876, 1988.

A Water-Stable Quadricyclane Derivative

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

A quadricyclane derivative stable in water was first synthesized. Valence isomerization between the quadricyclane and the corresponding norbornadiene was very clean, to be promising for a solar energy storage system.

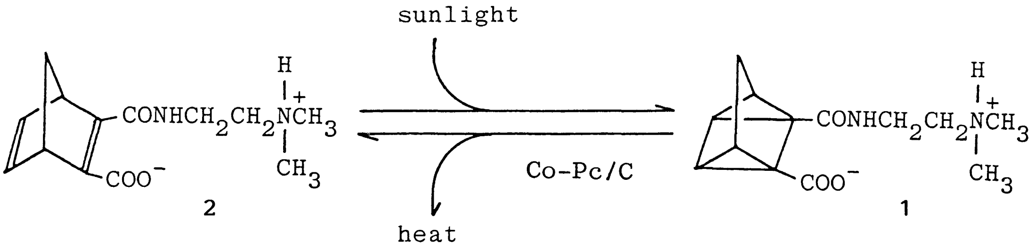
Quadricyclane is highly strained and more reactive than the valence-isomer norbornadiene. In particular, water easily added to quadricyclanes to give exclusively two isomers (Scheme 1).1) It is well-known that anhydrous solvents should be used in order to get quadricyclanes by photoisomerization of norbornadienes effectively. For the first time, we synthesized a quadricyclane derivative which was highly stable in water even without stabilizers.2)



Scheme 1. Hydration of quadricyclanes.

To an ice-cooled, dried dichloromethane solution of norbornadiene-2,3-dicarboxylic anhydride3b) was added dropwise N,N-dimethylethylenediamine with stirring to give white precipitates. The precipitates were collected by filtration, dried in vacuo, and recrystallized from a mixed solvent of dichloromethane and hexane to afford nearly quantitatively an analytically pure norbornadiene **2** as white plates (mp 224-226 °C). An aqueous solution of **2** was irradiated with a 300 W high-pressure mercury arc lamp through pyrex filter. After the completion of the photoreaction,5) the solution was evaporated to give a pure quadricyclane **1** as white powders without further purification.

In hot water, quadricyclane **1** was quite stable and could be stored for a long period. Exactly, refluxing an aqueous solution of **1** for 4 hours did not induce isomerization to the corresponding norbornadiene **2** nor addition of water to **1** (see Scheme 1) and led to exclusive recovery of **1**. By addition of small amount of cobalt phthalocycanine adsorbed on activated carbon (Co-Pc/C) to the solution even at room temperature, **1** isomerized to **2** rapidly, cleanly, and exothermically.6)



Scheme 2. A water-soluble solar energy storage system.

The valence isomerization between 1 and 2 in water (Scheme 2) is more effective[7)] than those in an aqueous alkaline solution reported so far,[3a)] which may be more promising for a solar energy storage system.

The present work was partially supported by a Grand-in-Aid for Scientific Research No. 62603013 from the Ministry of Education, Science and Culture.

References

1) S. J. Cristol and R. L. Snell, J. Am. Chem. Soc., 76, 5000 (1954); 80, 1950 (1958); F. A. Carroll, D. K. Green, and J. C. Sloop, Sol. Energy, 33, 377 (1984); K. Maruyama and H. Tamiaki, J. Org. Chem., 52, 3967 (1987); A. Behr, W. Keim, G. Thelen, H. -D. Scharf, and I. Ressler, J. Chem. Tech. Biotechnol., 32, 627 (1982).

2) In order to stabilize quadricyclanes in an aqueous solution, two improvements, additive effects were already reported; i) addition of bases kept the pH of the solution alkaline;[3)] ii) addition of cyclodextrin prevented quadricyclane from being in contact with water.[4)]

3) a) K. Maruyama and H. Tamiaki, Chem. Lett., 1982, 1699; K. Maruyama, H. Tamiaki, and T. Yanai, Bull. Chem. Soc. Jpn., 58, 781 (1985); b) K. Maruyama, H. Tamiaki, and S. Kawabata, J. Org. Chem., 50, 4742 (1985); c) K. Maruyama, H. Tamiaki, and S. Kawabata, Chem. Lett., 1984, 743; J. Chem. Soc., Perkin Trans. 2, 1986, 543.

4) T. Yumoto, K. Hayakawa, K. Kawase, H. Yamakita, and H. Taoda, Chem. Lett., 1985, 1021.

5) Determined by disappearance of the proton signals in the vinyl positions of 2 by ^{1}H NMR technique. Typically, 2 (0.1 mol dm^{-3}) isomerized to 1 quantitatively for 1 h (the quantum yield on irradiation with 313 nm light was 0.55.). In water, 2 could absorb sunlight (λ_{edge},[3b)] the wavelength where the extinction coefficient was unity, was 370 nm.) but 1 could not absorb sunlight (λ_{edge} = 300 nm). Therefore, irradiation with sunlight also induced the clean photoisomerization.

6) See Ref. 3c. Typically, 1 (0.1 mol dm^{-3}) isomerized to 2 quantitatively for 2 h by 10 g dm^{-3} of the insoluble catalyst (Co-Pc/C = 5 mg/1 g) at 25 °C.

7) In water, 1 might form an intramolecular salt due to both carboxyl and amino groups in the molecule and was more soluble. Therefore, the stored energy per unit volume in the system is larger.

(Received August 24, 1988)