HIGHLY EFFICIENT VALENCE ISOMERIZATION BETWEEN NORBORNADIENE AND QUADRICYCLANE DERIVATIVES UNDER SUNLIGHT

Kazuhiro MARUYAMA\*, Kazutoshi TERADA, and Yoshinori YAMAMOTO Department of Chemistry, Faculty of Science, Kyoto University, Kyoto 606

3-Phenylcarbamoyl-2,5-norbornadiene-2-carboxylic acid (1b) undergoes a facile and quantitative isomerization into the corresponding quadricyclane derivative (2b) under sunlight. The back isomerization of 2b to 1b proceeds quantitatively by the use of catalytic amounts of Rh<sub>2</sub>(CO)<sub>4</sub>Cl<sub>2</sub>.

Recently the photochemical solar energy storage into highly strained organic molecules has aroused an interest of many chemists. Valence isomerization between norbornadiene and quadricyclane is one of the most promising systems.<sup>1)</sup>



Unfortunately, however, either the utilization of an appropriate sensitizer or the introduction of substituents is required to realize a facile isomerization under sunlight, since norbornadiene itself, la, does not absorb solar radiation (>300nm) Recently we reported that the photoisomerization of la to 2a in the visible region was catalyzed by certain copper(I)-nitrogen ligand complexes.<sup>3)</sup>

We now wish to report an alternative approach, in which 3-phenylcarbamoyl-2,5-norbornadiene-2-carboxylic acid (1b) undergoes a facile valence isomerization into the corresponding quadricyclane derivative under sunlight. Although norbornadiene derivatives with relatively simple substituents are known to isomerize to the corresponding quadricyclanes photochemically, almost all of them do not absorb above 350nm.<sup>4)</sup> To solve this problem, we introduced arylcarbamoyl or arylimide groups to norbornadiene skeleton.<sup>5)</sup>



Norbornadiene derivatives,  $lb \sim lf$ , had a strong absorption in the near ultraviolet region and a tail until the visible region (Fig. 1), and hence they exhibited pale yellow color. In contrast to  $lb \sim lf$ , dimethoxycarbonyl derivative (lg), which was known to isomerize to the corresponding quadricyclane, <sup>4b)</sup> had only a weak absorption in the ultraviolet region (<350nm) (Fig. 1).

Acetonitrile solutions of norbornadiene derivatives,  $1b\sim 1f$ , (0.01-0.02M) were irradiated with a high pressure mercury lamp in a pyrex tube for 5-15h under argon or nitrogen atmosphere to afford the corresponding quadricyclanes,  $2b\sim 2f$ , in high yields (Table 1).<sup>5)</sup> Especially, 1b isomerized to 2b nearly quantitatively, which was highly promising for a solar energy storage system. Photoisomerization of 1b to 2b was followed by UV spectrum (Fig. 2).

Clean isomerization was recorded and isosbestic points were observed at 229 and 274nm. Quantum yields of photoisomerization for 1b~1f, which were measured at 313 or 366 nm, were relatively small (Table 1). Quantum yield for 1b is diminished about onesixth compared with the reported value for 1g.<sup>4b)</sup> Fortunately, however, the isomerization of 1b to 2b was faster than that of 1g to 2g about 1.2 times under solar radiation (Table 2), presumably due to the strong absorption of 1b in the near ultraviolet region.



Fig. 1 UV spectra of norbornadiene derivatives. Solvent; acetonitrile.

|    | <sup>R</sup> 1    | <sup>R</sup> 2     | Yield of quadricyclane (%) <sup>a)</sup> | <b>₽</b> <sup>b)</sup> |
|----|-------------------|--------------------|--|------------------------|
| lb | CONHPh            | со <sub>2</sub> н  | ~100                                     | 0.09                   |
| lc | CON               | (Ph)CO             | 85                                       | 0.07 <sup>C)</sup>     |
| 1d | CON (l-na         | aphthyl)CO         | 78                                       | 0.12                   |
| le | CONHPh            | CO <sub>2</sub> Me | 96                                       | 0.03                   |
| lf | CONHPh            | CONHPh             | 92                                       | 0.02                   |
| lg | CO2 <sup>Me</sup> | CO2Me              | 100 <sup>d)</sup>                        | 0.51 <sup>d)e)</sup>   |

Table 1 Photoisomerization of norbornadiene derivatives to the corresponding quadricyclanes

a) Determined by <sup>1</sup>H NMR spectra at 78-100% conversion, based on consumed 1. b) At 366nm. c) At 313nm. d) Reference 4b). e) At 314nm.

is the most effective system under solar radiation. Norbornadiene itself did not isomerize under this condition, because it cannot absorb solar irradiation.

It is known that back isomerization of quadricyclane derivatives to the corresponding norbornadienes is catalyzed by many transition metal complexes.<sup>6)</sup> For example, quadricyclanes, 2a and 2g, isomerize to the corresponding norbornadienes (1a and 1g) in the presence of  $Rh_2(CO)_4Cl_2$ .<sup>6c)6e)</sup> Actually this proved to be practical in our system; quadricyclane derivatives,  $2b\sim 2f$ , isomerize to  $1b\sim 1f$  by  $Rh_2(CO)_4Cl_2$  catalyst at room temperature. These back isomerizations



Table 2 Photoisomerization of norbornadiene derivatives under solar irradiation<sup>a)</sup>

| Norbornadiene | Convers | ion (%)<br>- \\ |
|---------------|---------|-----------------|
| 1b            | 89      | 70              |
| lg            | 71      | 59              |
| la            | 0       | 0               |

a) An acetonitrile solution of
0.02M of norbornadienes was
irradiated in a pyrex tube in
Kyoto. b) On 27 September in 1980,
a cloudy day, for 7h. c) On 9
October in 1980, a fine day, for
lh.

Fig. 2 UV spectra of photoisomerization of 1b to 2b. An acetonitrile solution of 1.13 X  $10^{-4}M$  of 1b was irradiated with 313nm light.

proceed nearly quantitatively. Consequently, it is clear that the most efficient valence isomerization system among norbornadiene derivatives, in a practical sense, is now at our disposal.



Acknowledgment. Financial support from the Ministry of Education, Science and Culture (Grant-in-Aid No. 505026) is gratefully acknowledged.

## References and note

- a) T. Laird, Chem. and Ind., <u>1978</u>, 186; b) H.-D. Scharf, J. Fleischhauer, H. Leismann, I. Ressler, W. Schleker, and R. Weitz, Angew. Chem. Int. Ed. Engl., <u>18</u>, 652 (1979).
- 2) a) K. B. Wiberg and H. A. Connon, J. Am. Chem. Soc., <u>98</u>, 5411 (1976); b) also see D. S. Kabakoff, J.-C. G. Bunzli, J. F. M. Oth, W. B. Hammond, and J. A. Berson, J. Am. Chem. Soc., <u>97</u>, 1510 (1975).
- 3) K. Maruyama, K. Terada, Y. Naruta, and Y. Yamamoto, Chem. Lett., 1980, 1259.
- 4) a) W. L. Dilling, Chem. Rev., <u>66</u>, 373 (1966); b) von G. Kaupp and H. Prinzbach, Helv. Chim. Acta, <u>52</u>, 956 (1969); c) H. Prinzbach, Pure and Appl. Chem., <u>16</u>, 17 (1968); d) von G. Kaupp and H. Prinzbach, Liebigs Ann. Chem., <u>725</u>, 52 (1969);
  e) J. R. Edman, J. Org. Chem., <u>32</u>, 2920 (1967); f) J. R. Edman and H. E. Simmons, J. Org. Chem., <u>33</u>, 3808 (1968).
- 5) All norbornadiene and quadricyclane derivatives were fully characterized by spectral analyses and gave satisfactory elemental analyses.
- 6) a) K. C. Bishop III, Chem. Rev., <u>76</u>, 461 (1976) and references cited therein;
  b) H. Hogeveen and H. C. Volger, J. Am. Chem. Soc., <u>89</u>, 2486 (1967); c) H.
  Hogeveen and B. J. Nusse, Tetrahedron Lett., <u>1973</u>, 3667; d) R. Noyori, I. Umeda,
  H. Kawauchi, and H. Takaya, J. Am. Chem. Soc., <u>97</u>, 812 (1975); e) H. Hogeveen
  and B. J. Nusse, Tetrahedron Lett., <u>1974</u>, 159; f) R. B. King and R. M. Hanes,
  J. Org. Chem., <u>44</u>, 1092 (1979) and references cited therein.

(Received March 9, 1981)