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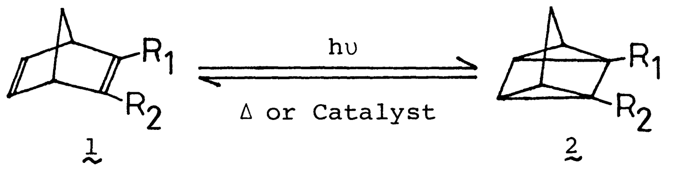
HIGHLY EFFICIENT VALENCE ISOMERIZATION BETWEEN NORBORNADIENE AND QUADRICYCLANE DERIVATIVES UNDER SUNLIGHT

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 $Rh_2(CO)_4Cl_2$.

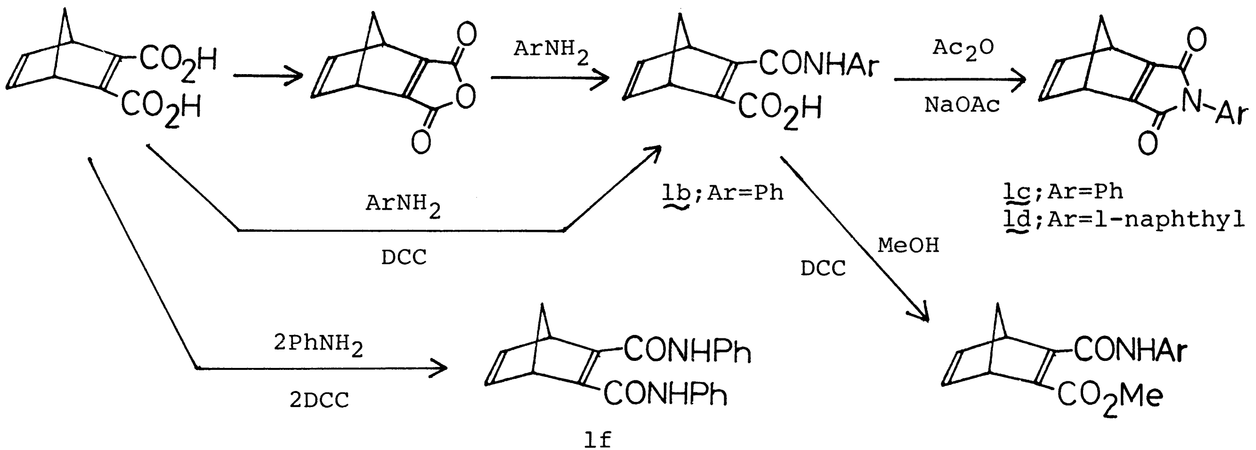
Recently the photochemical solar energy storage into highly strained organic molecules has aroused an interest of many chemists. Valence isomerization between norbornadiene and quadricyclane is one of the most promising systems.$^{1)}$



1a; $R_1=R_2=H$;
$\Delta H_{2a\rightarrow 1a}=-26$kcal/mol $^{2)}$

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, 1a, does not absorb solar radiation (>300nm) Recently we reported that the photoisomerization of 1a to 2a in the visible region was catalyzed by certain copper(I)-nitrogen ligand complexes.$^{3)}$

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.$^{4)}$ To solve this problem, we introduced arylcarbamoyl or arylimide groups to norbornadiene skeleton.$^{5)}$



1b;Ar=Ph

1c;Ar=Ph
1d;Ar=1-naphthyl

1f

1e;Ar=Ph

Norbornadiene derivatives, **1b**∼**1f**, 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 **1b**∼**1f**, dimethoxycarbonyl derivative (**1g**), which was known to isomerize to the corresponding quadricyclane,$^{4b)}$ had only a weak absorption in the ultraviolet region (<350nm) (Fig. 1).

Acetonitrile solutions of norbornadiene derivatives, **1b**∼**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**∼**2f**, in high yields(Table 1).$^{5)}$ 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 one-sixth compared with the reported value for **1g**.$^{4b)}$ 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. Therefore, to the best of our knowledge, **1b**

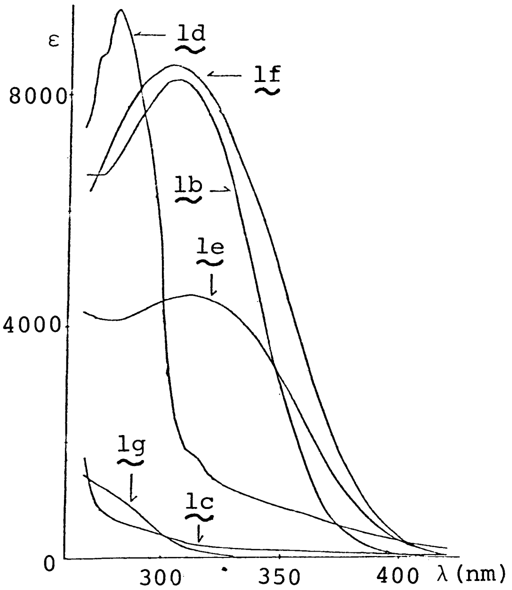


Fig. 1 UV spectra of norbornadiene derivatives. Solvent; acetonitrile.

Table 1 Photoisomerization of norbornadiene derivatives to the corresponding quadricyclanes

	R_1	R_2	Yield of quadricyclane (%)[a]	Φ[b]
1b	CONHPh	CO_2H	~100	0.09
1c	CON(Ph)CO		85	0.07[c]
1d	CON(1-naphthyl)CO		78	0.12
1e	CONHPh	CO_2Me	96	0.03
1f	CONHPh	CONHPh	92	0.02
1g	CO_2Me	CO_2Me	100[d]	0.51[d)e)]

a) Determined by ^1H 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.[6)] For example, quadricyclanes, 2a and 2g, isomerize to the corresponding norbornadienes (1a and 1g) in the presence of $Rh_2(CO)_4Cl_2$.[6c)6e)] Actually this proved to be practical in our system; quadricyclane derivatives, 2b~2f, isomerize to 1b~1f by $Rh_2(CO)_4Cl_2$ catalyst at room temperature. These back isomerizations

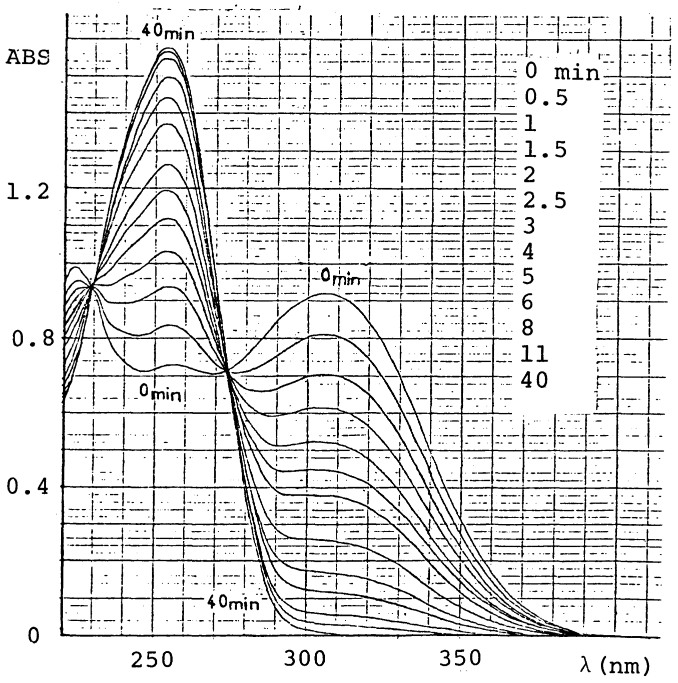


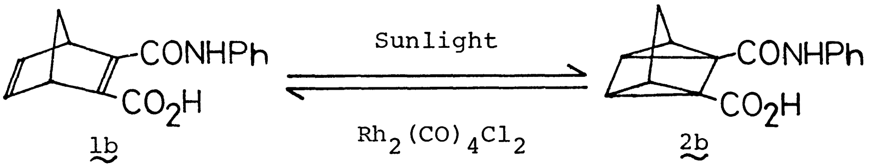
Fig. 2 UV spectra of photoisomerization of 1b to 2b. An acetonitrile solution of 1.13 X 10^{-4}M of 1b was irradiated with 313nm light.

Table 2 Photoisomerization of norbornadiene derivatives under solar irradiation[a]

Norbornadiene	Conversion (%) ⛅ 7h[b]	 ☀ 1h[c]
1b	89	70
1g	71	59
1a	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 1h.

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.



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