Valence Isomerisation between Coloured Acylnorbornadienes and Quadricyclanes as a Promising Model for Visible (Solar) Light Energy Conversion

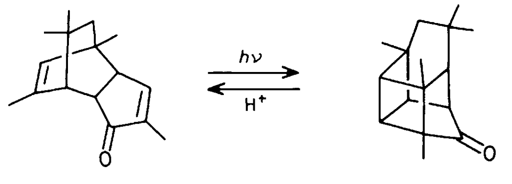
Ken-ichi Hirao, Akira Ando, Tatsuo Hamada, and Osamu Yonemitsu*

Faculty of Pharmaceutical Sciences, Hokkaido University, Sapporo 060, Japan

Among many coloured norbornadienes which have been synthesised bearing electron-donating and electron-withdrawing substituents, the 2,3-diphenyl-5-methoxycarbonyl-6-propionyl derivative was found to satisfy many important requirements for the chemical conversion of solar light energy because of its visible light absorption, a high quantum yield for its photocycloaddition to the corresponding quadricyclane, and a rapid and complete reversion of the quadricyclane to the norbornadiene with an acid catalyst.

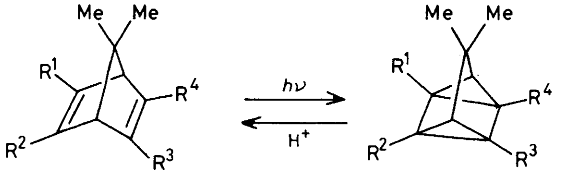
Many valence isomerisations of organic molecules have been proposed as model systems for the chemical conversion of light energy. Among them, the norbornadiene–quadricylane system has been widely investigated as one of the most promising models.[1–4] Although this system has its inherent advantages, improvements are required concerning the wavelength of light absorption of norbornadienes, the catalyst for the reversion of quadricyclanes, *etc.* We have previously reported[5] an original model consisting of the photocycloaddition of the carbonyl-containing Diels–Alder adducts of type (**1**) to provide the strained pentacyclic cage ketones (**2**) and their ready acid-catalysed reversion to (**1**), triggered by the protonation at the carbonyl group (see Scheme 1).

The principle of this valence isomerisation has now been extended to the norbornadiene–quadricyclane system. The norbornadienes (**3**) and (**7**), which efficiently absorb visible light,[2] were first synthesised by the Diels–Alder addition between the cyclopentadienes (**5**) and (**9**) bearing electron-donating groups (Me, Ph, p-MeOC$_6$H$_4$) and the acetylenes (**6**) bearing electron-withdrawing groups (CO$_2$Me, CONHPh, COEt, CN). All the norbornadienes (**3**) and (**7**) which were synthesised are coloured and their absorption spectra show a



(1) (2)

Scheme 1



(3) (4)

	R¹	R²	R³	R⁴
a;	Me	Me	CO_2Me	CO_2Me
b;	Me	Ph	CO_2Me	CO_2Me
c;	Me	Ar	CO_2Me	CO_2Me
d;	Ar	Ar	CO_2Me	H
e;	Ar	Ar	CO_2Me	CO_2Me
f;	Me	Ar	CONHPh	CONHPh
g;	Ar	Ar	CONHPh	CONHPh
h;	Me	Me	COPh	H
i;	Ar	Ar	COPh	H
j;	Ar	Ar	COEt	CO_2Me

Ar = p-$MeOC_6H_4$

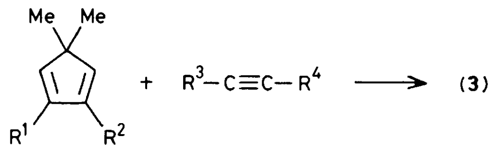
Table 1. Physical data for the valence isomerisation between the norbornadienes (**3**) and (**7**) and the quadricyclanes (**4**) and (**8**).

Compd.	A.E.[a]	φ[b]	Compd.	$t_{1/2}$[c]	k_m[d]
(**3a**)	441	0.66	(**4a**)	Stable	7.14×10^{-3}
(**3b**)	474	0.71	(**4b**)	Stable	
(**3c**)	526	0.26	(**4c**)	44	
			(**4d**)	0.8	
(**3e**)	554	0.08	(**4e**)	7.3	
(**3f**)	528	0.28	(**4f**)	>100	
(**3g**)	559	0.05	(**4g**)	13	
(**3i**)	527				
(**3j**)	581				
(**7a**)	487	0.56	(**8a**)	Stable	1.15×10^{-3}
(**7b**)	558	0.75	(**8b**)	Stable	1.32

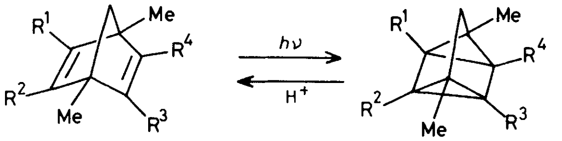
[a] Absorption edge (nm) in benzene. [b] Quantum yield at 383 nm. [c] Half-life (in h) in benzene at 20 °C. [d] Rate constant for the reversion with trifluoroacetic acid (TFA) in benzene at 32.0 ± 0.1 °C, $k_m = k_{obs}/(\text{M of TFA})$.

significant bathochromic shift with an absorption edge above 440 nm due to intramolecular charge transfer interaction between the electron-rich and electron-deficient double bonds[2] (Table 1).

On irradiation with light of wavelength above 300 nm, except for (**3h**—**j**), compounds (**3**) and (**7**) gave quantitatively the corresponding quadricyclanes (**4**) and (**8**). Quantum yields of the photocycloaddition, measured at 383 nm, varied with the substituents (Table 1). Methyl and/or phenyl substituted derivatives (**3a, b**) and (**7a, b**) showed quite high quantum yields, but the introduction of *p*-methoxyphenyl substituents, (**3c**—**g**), considerably decreased the efficiency of the photocycloaddition although it shifted the absorption markedly to quite longer wavelengths. In addition, (**4c**—**g**) to a greater or lesser extent were unstable at room temperature and reverted

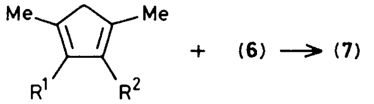


(5) (6)

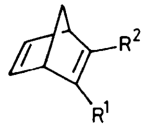


(7) (8)

	R¹	R²	R³	R⁴
a;	Ph	Ph	CO_2Me	CO_2Me
b;	Ph	Ph	COEt	CO_2Me
c;	Ph	Ph	COEt	CN



(9)



(10)

	R¹	R²
a;	COMe	H
b;	COPh	H
c;	COEt	CO_2Me

to the corresponding norbornadienes (**3c**—**g**) with the half-lives given in Table 1, whereas (**3a, b**) and (**7a, b**) with methyl and/or phenyl groups were stable in the absence of an acid-catalyst (Table 1).

The electron-withdrawing groups had no deleterious effect on the quantum efficiency, and moreover the introduction of the acyl groups caused a marked bathochromic shift in the absorption spectra; *e.g.* the absorption edge for (**7b**) was above 550 nm, even without a *p*-methoxyphenyl substituent.

According to the proposed mechanism for the acid-catalysed reversion of the pentacyclic cage ketones (**2**),[5] the reversion of the quadricyclanes (**4**) and (**8**), particularly with a ketone group,† was also expected to be accelerated by acid-catalysts. In fact, (**4a, b**) and (**8a**), bearing methyl, phenyl, and methoxycarbonyl groups, reverted smoothly and quantitatively to the corresponding norbornadienes (**3a, b**)

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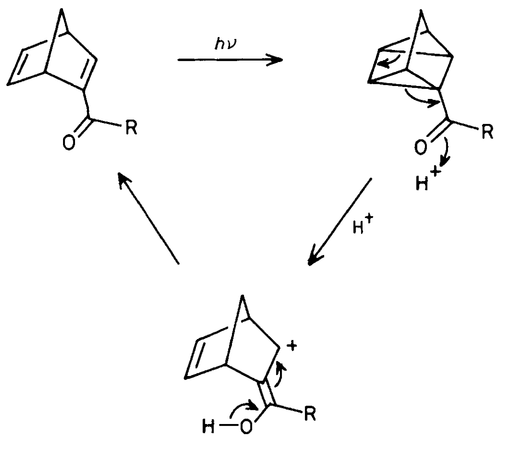
† Several acylnorbornadienes, (**3h**—**j**), (**7b, c,**) and (**10a**—**c**), were synthesised and their photoreaction and reversion examined. Unfortunately, none except (**7b**) was found to be practically useful. No photocycloaddition of (**3h**—**j**) occurred. Compound (**7c**) smoothly gave (**8c**), which, however, was not sufficiently stable at room temperature and gradually reverted to the starting (**7c**). Compounds (**10a, b**) were unstable at room temperature, although on irradiation the photoreaction seemed to proceed. The photocycloaddition of (**10c**) proceeded quite rapidly and efficiently with a high quantum yield of 0.82, but the absorption edge in the spectrum was only around 400 nm.



Scheme 2

and (**7a**) with trifluoroacetic acid or solid phosphoric acid[‡] in benzene at room temperature. The reversion of the *p*-methoxyphenyl substituted quadricyclanes (**4c**—**g**) occurred almost instantaneously and quantitatively to give (**3c**—**g**) under the same conditions.[§]

The acylquadricyclane (**8b**), which is stable without a catalyst, also reverted instantaneously and quantitatively to (**7b**) because the ketonic carbonyl group was the best trigger for the acid-catalysed reversion, as shown in Scheme 2.

In conclusion, (**7b**) is the most promising of all the compounds synthesised in this report for the reversible storage of visible light energy because of the following features: (i) the absorption of a fairly wide range of visible light by (**7b**);[¶] (ii) the high quantum yield for the photocycloaddition of (**7b**) to (**8b**); (iii) the efficient and rapid reversion of (**8b**) to (**7b**) with an acid-catalyst; and (iv) the high stability of both (**7b**) and (**8b**) in the absence of a catalyst.

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[‡] The industrial solid acid, phosphoric acid on silica gel, was activated by heating at 130 °C.

[§] The observed enthalpy of the isomerization of quadricyclane to norbornadiene was reported to be $\Delta H = -21.2 \pm 0.2$ kcal/mol (1 cal = 4.184 J).[6]

[¶] On irradiation with light of wavelength above 400 nm (halogen lamp with Toshiba L-42 filter), (**7b**) readily and quantitatively gave (**8b**). This photoreaction also proceeded with light of wavelength 410 and 463 nm as shown by use of a monochromatic irradiator.