Photochemical Formation of Strained Cage Compounds and their Acid-catalysed Reversion as a Preliminary Model for Light Energy Conversion

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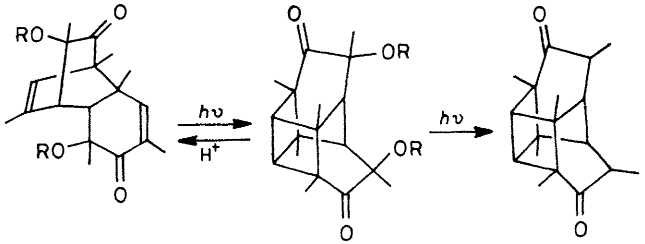
Summary On irradiation, some Diels–Alder adducts derived from cyclic dienes and dienones gave, quantitatively, strained pentacyclic C_{12}, C_{11}, and C_{10} cage compounds, which rapidly and completely reverted to the starting compounds with the evolution of heat (18·0—23·5 kcal/mol) when treated with an acid; the C_{11} system was found to be the most promising for the reversible storage of light energy.

SEVERAL years ago we reported that on irradiation, the Diels–Alder dimer (**1a**) readily gave the pentacyclododecanedione (**2a**), C_{12} cage, which almost instantly reverted to (**1a**) in a quantitative yield when dissolved in trifluoroacetic acid.[1] This fact shows that the (**1**) ⇌ (**2**) system is a promising candidate for the reversible storage of light energy. However, it is necessary to make many modifications to satisfy the stringent requirements for use in an energy storage system.[2]

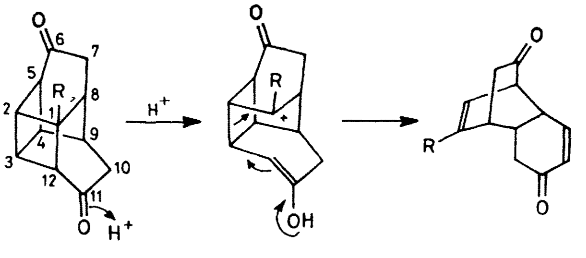


(1)
a; R = H
b; R = Me

(2)
a; R = H
b; R = Me

(2c)

We have now studied the photochemical conversion of several Diels–Alder adducts, easily synthesized from relatively simple compounds, into cage compounds and their acid-catalysed reversion in order to find the most promising system. Because (**2a**) is not very soluble in the usual organic solvents, it was converted into the *O*-methyl compound (**2b**), m.p. 107—108 °C. Treatment of (**2b**) in benzene with either a benzene-soluble acid such as trifluoroacetic acid and anhydrous toluene-*p*-sulphonic acid (TsOH) or an insoluble acid such as commercial cation-exchange resins and 'solid phosphoric acid'† at room temperature gave almost instantly (**1b**), m.p. 118—119 °C, in a quantitative yield. The heat of reaction (ΔH) measured on a twin micro-calorimeter was 20·0 ± 1·1 kcal/mol, and the rate constant with toluene-*p*-sulphonic acid, expressed as k_m (k_{obs}/M of the acid), was 0·54 s^{-1}. Thus, the (**2b**) → (**1b**) process proceeded very cleanly and rapidly, but unfortunately the photoreaction of (**1b**) was not clean because the Norrish Type II cleavage of (**2b**) by absorption of another photon to form (**2c**), m.p. 157·5—159 °C, was unavoidable especially in the final stage of the photoreaction.



(A) (B) (C) (1)

The mechanism of the acid-catalysed reversion is shown in equation (1).[1] The presence of an electron-donating group (R) at C-1 to stabilize an intermediary cation (B) is essential. Accordingly, we then synthesized (**3a**), m.p. 49—50 °C, and (**3b**), m.p. 44—46 °C, from (**5**)[3] and (**6**) *via* (**7**), and similarly (**3c**), m.p. 80—82 °C, and (**3d**), oil, from (**5**) and (**8**).[4]

When (**3a—d**) in benzene were irradiated with a high pressure mercury lamp using a Pyrex filter, a very clean photoreaction occurred to give the corresponding pentacycloundecanones (**4a—d**), C_{11} cages, in quantitative yields. This photoreaction proceeded quite smoothly with light of wavelengths at least up to 360 nm as shown by use of a monochromatic irradiator. The quantum yields for the formation of (**4a**), (**4b**), (**4c**), and (**4d**) at 320 nm were 0·34, 0·34, 0·29, and 0·30, respectively. The acid-catalysed reversion of (**4a**) with toluene-*p*-sulphonic acid in benzene proceeded quantitatively at room temperature and the observed heat of reaction was 21·7 ± 1·1 kcal/mol. The energy storage efficiency (*Q* value)[5] at 320 nm is therefore calculated to be 8·3%. Acid treatment of (**4a—d**) gave, also quantitatively, the corresponding compounds (**3a—d**) with observed reaction heats of 22·6, 23·5, and 21·9 kcal/mol respectively. The reversion of (**4**) proceeded very rapidly, *e.g.*, k_m (TsOH) values for (**4b**) and (**4d**) were 0·8 and 10·8 s^{-1}, respectively.

The (**3**) ⇌ (**4**) (C_{11} cage) system appears to be very close to the (**9**) ⇌ (**10**) (C_{10} cage) reaction,[6] but there is a definite difference between the two systems, because no satisfactory method for the reversion (**10**) → (**9**) has been found.

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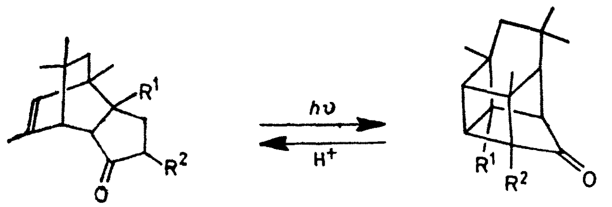
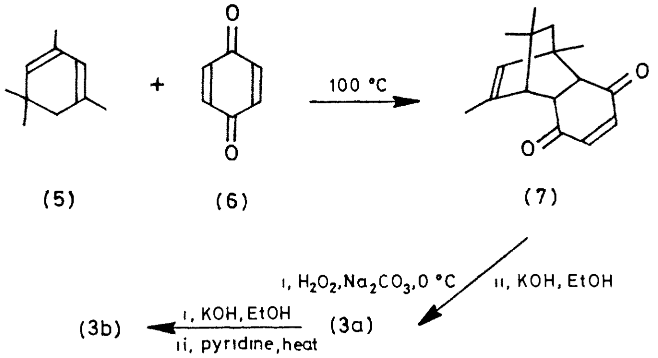
† The commercially available industrial solid acid, phosphoric acid on silica gel, was activated by heating at 130 °C.

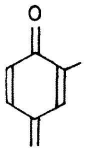


(3) (4)

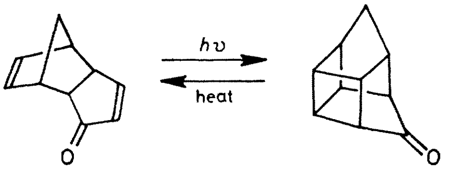
a; $R^1 = CO_2Et$, $R^2 = H$
b; $R^1 = R^2 = H$
c; $R^1 = CO_2Me$, $R^2 = Me$
d; $R^1 = H$, $R^2 = Me$



(5) (6) (7)

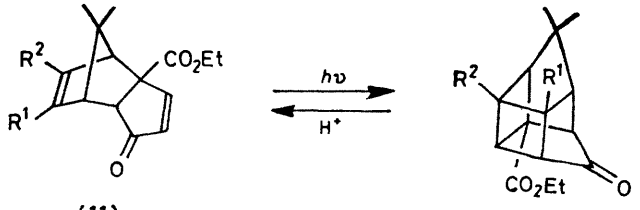


(8)



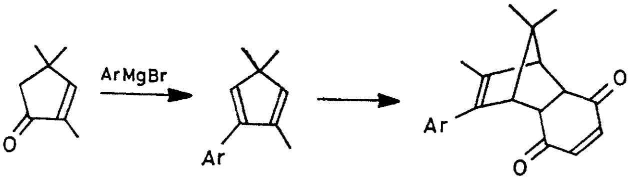
(9) (10)

Moreover, a number of currently proposed reversible reactions including the well known norbornadiene–quadricyclane interconversion still require an efficient reversion method which uses a stable and inexpensive (solid) catalyst.[7]



(11) (12)

a; $R^1 = p\text{-}MeOC_6H_4$, $R = Me$
b; $R^1 = Me$, $R^2 = p\text{-}MeOC_6H_4$



(13) (14) (15)

$Ar = p\text{-}MeOC_6H_4$

As a preliminary model which absorbs light of longer wavelengths (**11a**), m.p. 95—96·5 °C, and (**11b**), m.p. 93—94 °C, were synthesized from (**13**)[8] and (**6**). On irradiation with light of wavelength at least up to 390 nm, (**11a**, **b**) readily gave pentacyclodecanones (**12a**, **b**), C_{10} cages. ΔH values for (**12a**) and (**12b**) were 18·0 and 18·7 kcal/mol, respectively, and k_m for (**12b**: $R^1 = Me$) was only $8{\cdot}0 \times 10^{-4}\ s^{-1}$. Compound (**12a**: $R = C_6H_4OMe$) again rapidly reverted to (**11a**) with a k_m value of $1{\cdot}2\ s^{-1}$.

There are two immediate advantages resulting from the introduction of the *p*-methoxyphenyl-group as R^1: (i), a shift to longer wavelengths of absorption bands in Diels–Alder adducts and (ii), a marked acceleration of the acid-catalysed reversion of cage compounds. In conclusion, the C_{11} system was found to be the most promising system for the reversible storage of light energy because of its large ΔH and k_m values as well as its easy synthesis and modification.‡

We thank Professor K. Tanabe for his kind advice on solid acids and Professor S. Sugai for reaction heat measurements.

(*Received*, 16*th April* 1980; *Com.* **393**.)

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‡ The calculated strain energy difference for the C_{11} ring system is somewhat larger than those for the C_{12} and C_{10} systems: E. Ōsawa, K. Aigami, and Y. Inamoto, *J. Org. Chem.*, 1977, **42**, 2621.

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