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PHOTOCHEMICAL BEHAVIOR OF BRIDGED COMPOUNDS. *VII*[1]. NON-DISSOCIATING CYCLOPENTADIENONE-DIMERS

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We have recently reported on the variegated photochemical reaction modes of cyclopentadienone-dimers. While the parent, unsubstituted system has been more thoroughly investigated[1,2] and found to follow three conversion paths *of the type* $I \rightleftharpoons II + III + IV$, substituted derivatives appeared[3] to undergo peculiar transformations according to whether they were reversibly dissociating or irreversible (stable) cyclopentadienone-dimers[4]. To gain insight into the rather subtle behavior of these two classes of compounds we have decided to study them separately. Hence, this report deals with non-dissociating, substituted cyclopentadienone-dimers, *viz.*, those derived from 3,4-diphenylcyclopentadienones *lacking* substituents in the 2 and/or 5 position[4].

While further pursuing the investigation of *I*a[3], we also examined its dimethyl derivative, i.e. the dimer *I*b for reasons on which we shall elaborate in the full paper. *I*b (like the parent compound[1,2] and *I*a[3]) rearranges on irradiation[5a] to *II*b[6] and the latter, when irradiated[5a] returns to *I*b which, however (unlike in the above cases) is accompanied by another isomer in ca.7% yield, for which we propose the cage structure *IX*b[6]. Neither *III* nor *IV* were isolated in the photolyses of *I* (a and b).

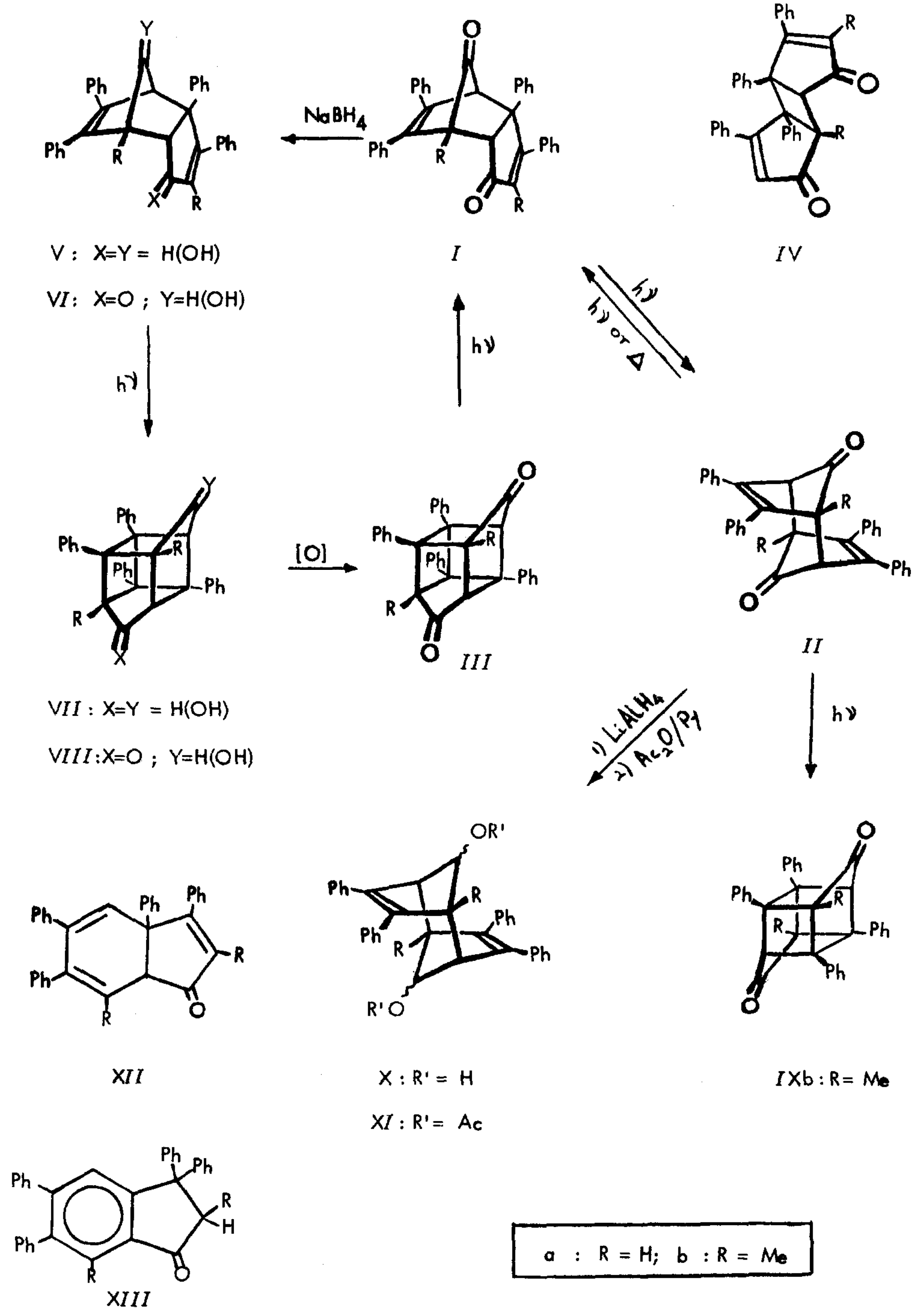
The cages *III* (a and b) were synthesized by an indirect route. $NaBH_4$ reduction of *I*a in methanol/dioxane yielded the diol Va[6] as a major product[7a,b] whereas *I*b gave the hydroxy ketone *VI*b[6,9]. On irradiation[5a], Va gave *VII*a[6], and *VI*b led to *VIII*b[6]. Eventually *III*a[6] and *III*b[6] were obtained by Jones oxidation of *VII*a and *VIII*b respectively. This series of events, besides making available the cages *III* proves the *endo*-configuration of the dimers *I* (which, incidentally, was similarly proven for the dissociating dimers[‡,8,7]).

Irradiation[5a] of the cages *III* (a and b) led to their rapid disappearance and *II*a and b were isolated accompanied by small amounts of their precursors *I*. Obviously, the greater photolability of *III* as compared to *II* accounts for the failure to detect the expected reverse process *I* ⟶ *III* in the irradiation of *I*.

Reduction ($LiAlH_4$) of *II*(a and b) followed by acetylation, gave X (a and b) and *XI* (a and b) respectively. Irradiation[5a] of the latter left them unchanged. This supports the structure *II* (symmetry C_i) since *syn*-diketones (symmetry C_2 or C_s) would be expected to undergo internal (2 x 2) cycloaddition to the corresponding (C_2 or C_s) cage diketones. These considerations enabled us to assign the tentative structure to *IX*b suggesting that it is formed in a $({}_{\pi}2 + {}_{\sigma}2 + {}_{\pi}2 + {}_{\sigma}2)$ pericyclic reaction of *II*b[10] (cf. also ref.8).

[‡] Taken in part from the M.Sc. Thesis of B.P., Tel-Aviv University, 1972.

SCHEME[6]


NaBH$_4$
hν
hν or Δ
1) LiAlH$_4$
2) Ac$_2$O/Py
[O]
Ph
R
V : X=Y = H(OH)
VI : X=O ; Y=H(OH)
I
IV
VII : X=Y = H(OH)
VIII : X=O ; Y=H(OH)
III
II
XII
X : R' = H
XI : R' = Ac
IXb : R = Me
XIII
a : R = H; b : R = Me

Finally, a note on the thermal behavior of *I* and *II*. Any attempt to detect a thermal, degenerate Cope rearrangement of *I* (a and b)[11a] failed. This is in contrast to the behavior of the unsubstituted dicyclopentadiene-8-one which readily rearranges to dicyclopentadiene-1-one[11b]. On the other hand, *II*b is pyrolysed in boiling bromobenzene to a mixture of *I*b and its decarbonylation product, dihydroindenone X*II*b whereas at>200°C, *II*(a and b) provides the known rearrangement product of X*II*, X*III* (a and b)[12].

Further conclusions that can be drawn so far: Both carbonyls are a must for the transformations $I \rightleftarrows II$ but none of them is necessary for the internal (2 + 2) cycloaddition, cf. Va — V*II*a. Moreover, the latter occurs without sensitization, in contrast to other known instances, e.g. dicyclopentadiene[13]; the stilbene moieties are apparently excited and undergo efficient intersystem crossing culminating with the collapse to the cage. Orbital symmetry control is not operating in some cases e.g. $II \xrightarrow{\Delta} I$, advocating non-concertedness but this is not necessarily so for all observed processes.

A detailed account and discussion including also quantum yields and quenching results are deferred to the full paper. It is worth mentioning though, that the photochemical processes (except the decarbonylation at 254 nm) proceed via triplet excited states.

TABLE[6]

Compound[a]	m.p., °C	ν_{max}^{KBr}, cm^{-1} [b]	τ (no.of protons, multiplicity)[c,d] H	Me
*II*a	257	1770		
*II*b	269-70	1760		
*III*a	116-7	1755	6.08(2,s); 6.93(2,s)	
*III*b	225	1760	7.03(1,s); 6.03(1,s)	9.36(3,s); 8.48(3,s)
Va	193-4	3500(3380)	4.3-6.3(7,m); 3.5(1,bs)[C']	
V*I*b	224-5	3400, 1670	8.07(1,d); 6.79(1,s); 5.93(1,dd); 5.76(1,d)	8.70(3,s); 8.22(3,s)
V*II*a	291-2	3520(3300)	4.4(2,bs); 5.1(2,bs); 5.9(2,bs); 6.3(2,bs)[C']	
V*III*b	162	3490(3300), 1750	7.95(1,bs); 6.90(1,s); 5.82(1,s); 5.45(1,bs)	9.28(3,s); 8.58(3,s)
*I*Xb	305	1750	6.03(2,s)	9.08(6,s)
Xa	297	3540(3400)	4.8(4,bm); 6.6(4,m)	
Xb	294	3550(3430)	7.0(2,d); 5.92(2,m); 4.88(2,d)	9.39(6,s)[C"]
X*I*b	305	1730	6.52(2,m); 4.73(2,m)	9.27(6,s); 8.1(6,s)

[a] The dimers *I*(a and b) are known[4,3] as are also the decarbonylation products X*II* (a and b)[4,11] and their structures were unequivocally confirmed by NMR spectroscopy. The photo-product *II*a was reported[3] but is listed here for the sake of comparison. [b] Only the C=O and O-H stretching frequencies are given. [c] The phenyl protons are not listed; s=singlet, d=doublet, m=multiplet, b=broad; the NMR spectra were measured in $CDCl_3$ unless otherwise stated: C') Pyridine-d_5, C") DMSO-d_6. Compounds *II* (a and b) were too insoluble for NMR measurements. [d] The UV spectra are not listed because of space scarcity but in all, the criterion of the stilbene absorption is fully obeyed, i.e. cages absorb only at low wavelengths while unsaturated dimers exhibit the 285 nm absorption.

REFERENCES and FOOTNOTES

1. Part *VI*: U.Klinsman, J.Gauthier, I.Schaffner, M.Pasternak and B. Fuchs, *Helv.Chim.Acta.* submitted for publication.

2. E. Baggiolini, E.G.Herzog, S.Iwasaki, R.Schorta and K.Schaffner, *Helv.Chim.Acta*, **50**, 297 (1967).

3. B. Fuchs, *J.Am.Chem.Soc.*, **93**, 2544 (1971).

4. M.A. Ogliaruso, M.Romanelli and E.S. Becker, *Chem.Rev.* **65**,261 (1965) and references cited therein.

5. Irradiation of deaerated solutions were performed in dioxane, acetonitrile or benzene solutions using a Rayonet reactor with 3000 Å lamps and Pyrex vessels.

6. All new compounds gave correct elemental analyses and molecular weights (mass spectrometrically). The physical data are assembled in the Table. Structural assignments were made on the strength of IR-(C=O, O-H and C=C stretching), UV-(isolated phenyl vs. *cis*-Stilbene absorptions), NMR-(bridgehead protons and methyl groups and symmetry considerations) and Mass spectral information as well as chemical behavior (see text).

7. a. K.N. Houk and D.J. Northington, *Tetrahedron Letters*, 303 (1972).

   b. These authors recently reported the same reaction to give the hydroxy-ketone *VIa* which in our hands was obtained as a minor product, albeit no comparison was possible since no physical properties, yields or structural proof were given for *VIa*, *VIIIa* and *IIIa*. In addition to that we were also miscited and misquoted. Thus, we have never contended that the transformation *I* ⟶ *II* occurs via an excited singlet state but quite the contrary[3] (cf. also ref.1). For further comments see the following paper[8].

8. B. Fuchs, M.Pasternak and B. Pazhenchevsky, following communication.

9. Interestingly, also a number of tetraalkyl-tetraphenyl (dissociating) dimers that we studied were reduced by $NaBH_4$ to hydroxy-ketones of type *VI*[8]. Steric effects are apparently operating since *Ia* is reduced to the diol as is also the unsubstituted cyclopentadienone-dimer (cf. K Hafner and K. Goliasch, *Chem. Ber.*, **94**, 2909 (1961).

10. R.B. Woodward and R. Hoffmann, *Angew.Chem.* **8**, 797 (1969).

11. a. The attempt was made by heating solutions of *I* in the NMR probe. No changes in the spectra of *I* (a and b) were observed up to their decarbonylation (cf. also ref. 1 for a similar behavior of the unsubstituted analog of *I*).

    b. R.C. Cookson, J. Hudec and R.O. Williams, *J.Chem.Soc.* (C), 1382 (1967).

12. a. C.F.H. Allen and J.A. Van Allan, *J. Org. Chem.*, **20**, 315 (1955).

    b. *id.*, *ibid.*, **14**,1051 (1949).

13. W.L. Dilling, *Chem.Rev.* **66**, 373 (1966).