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

Benzion Fuchs, Barak Pazhenchevsky and Mordechai Pasternak
Department of Chemistry, Tel-Aviv University, Tel-Aviv, Israel.

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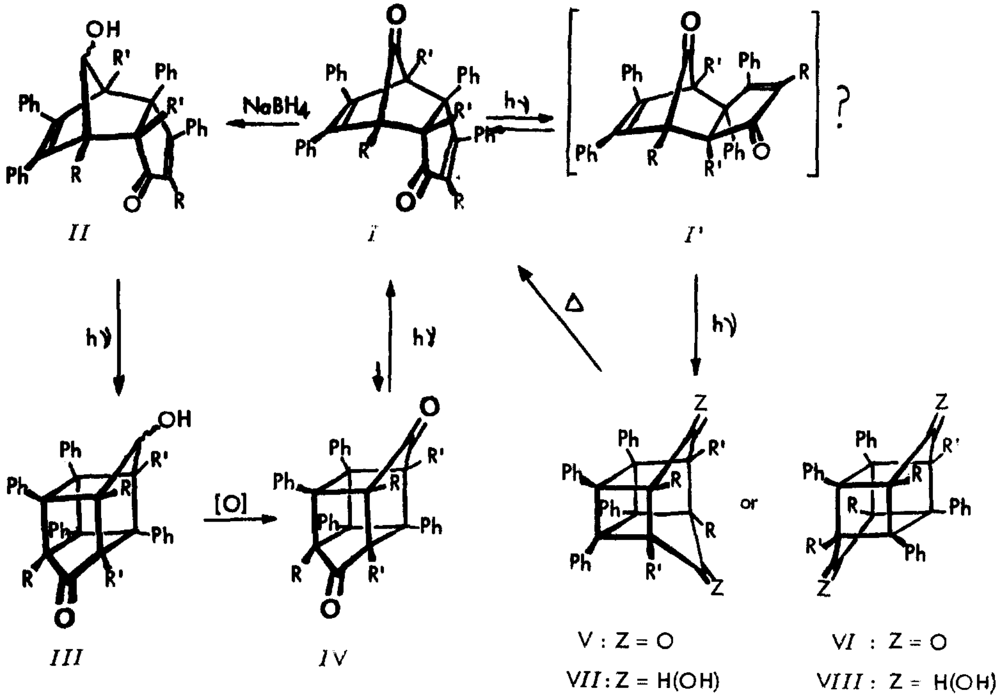
Since our first observations in this field[2], a communication that has recently appeared in this Journal[3] prompted us to report at this stage further results of our own work on the title subject i.e. thermal and photochemical transformations of dissociating, substituted cyclopentadienone-dimers (see Scheme and Table 1). Parallel results on non-dissociating dimers are the subject of two former parts in this series[1,4].

We have previously concluded[2] that the dimer *I*a photo-rearranges to symmetric cage products and rationalized this by suggesting that *I*a has exo configuration. We proceeded to investigate this point also by extending our research to other analogs of *I*a, viz. with R=Me and R'= Et, Pr[5] and found that both *I*a and *I*b are, in fact, endo-dimers in their thermally stable form as demonstrated by the sequence of reactions $I \rightarrow II \rightarrow III \rightarrow IV$[6,7]. The structure of the dimer *I*b as well as that of *I*c (R=Me, R'=Pr) were proven in an NMR spectroscopic, comparative study of a series of dimers *I* bearing methyl substitutents in various positions (see Table 2), which implicitly confirms also the endo-configuration of all these dimers i.e. the dissociating and the non-dissociating[1] ones.

Turning now to the photochemical aspects, *I*a, as reported[2], is converted by irradiation[8a] into a minor product, the dissymmetric cage *I*V and in major yield to a symmetric cage which is high melting, insoluble and unreactive to a variety of reagents but can be reduced by $LiAlH_4$ in boiling tetrahydrofuran to a symmetric dihydroxy derivative and not to a hemiketal as thought before[2,9]. This development actually reintroduces ambiguity in the structural assignment to the symmetric photoproduct of *I*a since both the C_{2v} structure V and the D_{2h} structure V*I* can accommodate the reported physical properties[2,6]. Up to now, all attempts to solve this problem by chemical reactions of either the diketone or the diol failed, apparently because of their extreme unreactivity which is probably due to steric hindrance and low solubility. This crucial point is now being intensively investigated in these laboratories, including X-ray diffraction. It seems to us, though, that either way, since no unsaturated, centrosymmetrical photo-product is isolated (as is in the case of non-dissociating dimers[1]), transient, thermally labile exo-species *I*' might be involved in this transformation. In the series R=Me, R'= Et the conversion *I*b → Vb (or V*I*b) likewise occurs but only at lower temperatures (~ 5°), the next homolog *I*c (R=Me, R'=Pr) fails however to photolyze even at low temperatures. Two effects are apparently operative. One consists in the inhibiting influence of the monomer on the extent of reaction and lowering the temperature was thought to reduce its concentration to a minimum; the second is of steric origin, viz. bulky substitutents in the 1,4,6 and 7 position of *I* should evidently obstruct the rotation of the two molecule-halves around the 6,7 bond after the 1,2 bond cleavage[11].

SCHEME[6]



a : R = R' = Me; b: R = Et, R' = Me

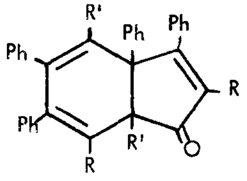
TABLE *I*

Compound[a]	*I*a	*I*b	*II*a	*II*b	*III*a	*III*b	*IV*a	*IV*b	Va	Vb	*VII*a	*IX*a	*IX*b
m.p., °C	183-4	136	185-6	191	296-7	278	318	220	272	205	320	166	144
ν_{max}^{KBr}, cm^{-1} [b]	1765 1690	1770 1690	3480 1670	3460 1670	3420 1740	3500 1780	1750	1740	1750	1750	3550 (3430)	1710	1705
τ_{Me} (No. of protons; all singlets)	7.75(3) 8.35(3) 8.75(3) 9.42(3)	8.40(3) 9.40(3)	7.90(3) 8.25(3) 8.85(3) 9.10(3)	8.13(3) 9.02(3)	8.18(3) 8.40(3) 9.33(3) 9.50(3)	8.20(3) 9.30(3)	C' 8.20(6) 9.50(6)	8.2(3) 9.4(3)	C' 8.80(12)	C' 8.32(6)	C'' 8.90(12)	8.08(3) 8.45(3) 9.02(3) 9.23(3)	9.13(3) 9.27(3)

a) The dimers *I*a and *I*b are known[5] as is also *IX*a[5a,3] and the photoproduct Va[2]. The data are listed for the sake of comparison. b) Only the C=O and O-H stretching frequencies are given. c) Only the methyl groups on the ring are listed since they provide a good criterion for symmetry considerations. The NMR spectra were measured in $CDCl_3$ unless otherwise stated: C') hot chlorobenzene, C'') hot DMSO-d_6. d) The UV spectra are not listed but exhibit the expected absorptions.

Interestingly, *I*V (a and b) when irradiated[8a], are rapidly converted to V (or V*I*) accompanied by their respective precursor dimer *I* (a and b). Again[1] it appears that this photolability of *I*V is responsible for the fact that the formation of V (or V*I*) is overwhelmingly favored over *I*V in the irradiation of *I*.

It has been contended[3] that *I*Va is formed in a sensitized process in contrast to direct irradiation of *I*a, were Va is favored. This was based on the finding[3] that the formation of Va was inhibited by irradiating *I*a in acetone solution with 254 nm light, whereas *I*V was formed (in unspecified yield[3] - poor as usual, as we subsequently established). We duplicated these experiments both at 254 and 300 nm (since the combination of 254 nm light with acetone is not particularly appealing) and found that similar results were obtained in acetone solution as well as in dioxane solution <u>with acetone as an external filter</u>. Apparently, this is just another manifestation of the, often encountered, wave-length dependent behavior of these systems. In fact, we think that no sensitizer is needed in any of the photochemical processes of *I* since the cyclopentenone moiety undergoes efficient intersystem crossing to a high energy triplet (cf.ref.4 for a discussion of this point). Other mechanistic-photochemical data indicate indeed the intermediacy of triplet excited states in the above photochemical reactions and will be reported elsewhere as will also the results of investigations now in course, concerning temperature and wavelength dependence as well as substituent effects in these photoprocesses.



*I*X

Finally, short wavelength (254 nm) irradiation[7b] of *I* (a and b) provide the corresponding dihydroindenones *I*X (a and b)[6] which are obtained also by thermal decarbonylation albeit in much lower yield. Pyrolysis of V (or V*I*) in boiling bromobenzene yields back the dimers *I* evidently in a radical process.

TABLE 2

Chemical Shifts (τ) of Methyl Groups in Various Positions of I^a

I^b		Position			
R	R'	1	4	6	7
Me	Me	8.35	7.75	9.42	8.75
Me	H		7.80		8.66
Et	Me	8.40		9.40	
Pr	Me	8.35		9.40	

[a] The NMR spectra were taken on $CDCl_3$ solutions

[b] Only the ring methyls are listed.

REFERENCES and FOOTNOTES

1. Part *VII* in the series: B. Pazhenchevsky and B. Fuchs, preceeding communication.
2. B. Fuchs, J.Am.Chem.Soc. **93**, 2544 (1971).
3. K.N. Houk and D.J. Northington, Tetrahedron Letters, 303 (1972). cf. also footnote 7 in ref.1.
4. U. Klinsman, J. Gauthier, K.Schaffner, M.Pasternak and B. Fuchs, Helv.Chim.Acta., submitted for publication.

5.a. C.F.H. Allen and J.A.Van Allan, J.Am.Chem.Soc., **72**, 5165 (1950).

b. M.A. Ogliaruso, M.G. Romanelli and E.I. Becker, Chem.Rev., **65**, 261 (1965).

6. All new compounds gave correct elemental analyses and molecular weights (mass spectrometrically). Physical data are assembled in Table 1. Structural assignments were made on the strength of IR-(C=O), O-H and C=C stretching frequencies), UV-dimers *I* (cis-stilbene absorption in the isolated phenyl absorptions in saturated cages vs.) NMR-(methyl groups and symmetry considerations) and Mass spectral behavior.

7.a. The endo-configuration of *Ia* has been conjectured previously[7b] and recently proven in a similar way[3].

b. C.M. Anderson, I.W. McCay and R.N. Warrener, Tetrahedron Letters, 2735 (1970).

8. Irradiations of deaerated solutions were carried out in a Rayonet reactor as following: a) 3000 Å lamps Pyrex or quartz vessels, dioxane, benzene, acetonitrile or acetone (see text) solutions. b) 2537 Å lamps, quartz vessels, dioxane or acetonitrile solutions.
9. The faulty assignment stemmed from the following contingent occurrence: The mass spectrum of *VIIa* taken on a Hitachi-Perkin Elmer RMU-6 instrument exhibited the m/e 522 as its highest peak which was therefore interpreted as the molecular ion of the hemiketal (elemental analysis supported this but was of course in the same error range as that of the diol). Recently, the mass spectrum was measured on an Atlas CH4 instrument and revealed, to our surprise the m/e 522 and 524 peaks with equal intensity. Furthermore, lately we succeeded in taking an NMR spectrum of *VIIa* (*VIIIa*) in hot DMSO-d_6 which showed only one singlet for all methyl protons and hence the symmetric structure of the diol. Since dehydration attempts to symmetric cyclic ether failed we concluded that the exo, exo-diol *VIIa* or a centrosymmetric structure *VIIIa* obtains.

10.a. This hypothesis could find support in the known cyclopentadiene ⟶ exo-dicyclopentadiene, photochemical process[10b].

b. N.J. Turro and G.S. Hammond, J.Am.Chem.Soc., **84**, 2841 (1962).

11. For similar substituent effects on the mechanism of thermal rearrangements of related interest, cf. J.A. Berson and G.L. Nelson, J.Am.Chem.Soc., **92**, 1096 (1970).