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267. The Photochemical and Thermal Interconversion of Some Cyclopentadienone Dimers[1])

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Summary. In continuation of previous work on cyclopentadienone dimers [3], thermal and photochemical interconversions of the isomeric diketones **1**, **3**, and **5** by skeletal rearrangements have been established to the extent summarized in schemes 2 and 3, and the intramolecular [2+2] cycloaddition **1** → **2** was found to be reversible photochemically.

We have previously shown that UV. irradiation of dicyclopentadienone **1** results in an intramolecular [2 + 2] cycloaddition to the cage diketone **2** and in a rearrangement to product **3** [3] (scheme 1). The product ratio **2**:**3** had been found to vary with the excitation wavelength, using 2537 Å ($\pi \rightarrow \pi^*$ excitation) and $\geq$ 3130 Å ($n \rightarrow \pi^*$ excitation). On triplet sensitization with acetophenone the formation of product **2** was observed. Furthermore, a smooth thermal decarbonylation of **1** to **4** occurred at ca. 140° (in boiling xylene) (*cf.* also [4]).

[1]) Part 69 of the series 'Photochemical Reactions' (part 68, see [1]) and Part 6 of the series 'Photochemical Behaviour of Bridged Compounds' (part 5, see [2]).

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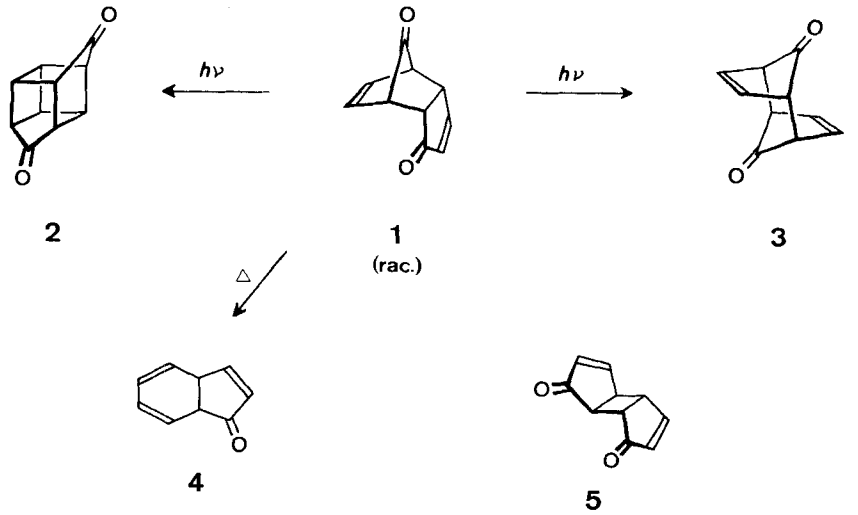
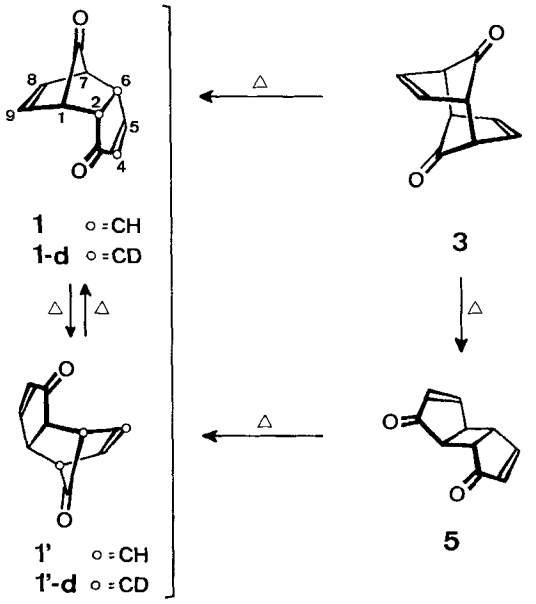
Scheme 1



We now report on more recent work with compounds **1–3** and the new isomer **5** which affords further insight into the photochemical and thermal relationships between these cyclopentadienone dimers.

Thermal Transformations of Compounds 1, 3, and 5. – The compounds **3** and **5** very cleanly undergo thermal rearrangements. In boiling carbon tetrachloride, **3** afforded ca. two parts **1** and one part **5** after 8 h. Partial thermolysis of a chloroform

Scheme 2. Thermal Rearrangements of Compounds **1**, **3** *and* **5**



solution of **5** in a sealed tube at 150° for 30 min and subsequent catalytic hydrogenation of the reaction mixture exclusively gave the tetrahydro derivatives of compounds **1** and **5** (= **11**).

Furthermore, the unsymmetrically deuteriated compounds **3**-d and **5**-d were prepared by acid-catalyzed deuteriation of **1** (**1**-d: 4% d_0, 20% d_1, 37% d_2, 29% d_3, 10% d_4), photorearrangement of **1**-d to **3**-d (*cf.* [3]), and thermal conversion of the latter to **1**-d and **5**-d. Compounds **1**-d and **4**-d, which were obtained on heating **3**-d and **5**-d, respectively, and were analyzed by mass spectrometry, quantitatively exhibited in each case the same isotopic composition as the starting compounds[3]).

While the NMR. spectrum of compound **1** in hexachlorobutadiene solution on heating from 22°–140° remained unchanged up to 120° when decarbonylation to **4**

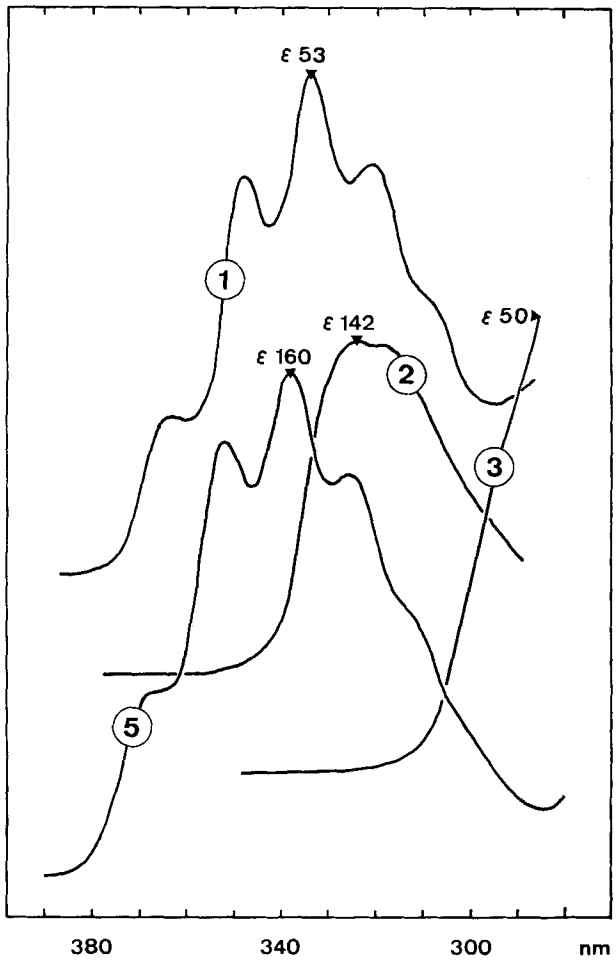


Figure 1. *UV. absorption spectra* (region of $n \rightarrow \pi^*$ transitions) *of compounds* **1–3** *and* **5** *in benzene solution*

[3]) We thank Dr. *B. Willhalm*, Firmenich & Cie. for the mass spectrometric determinations.

began, a similar investigation of **1**-d (14% d_0, 33% d_1, 33% d_2, 16% d_3, 4% d_4) at 90° revealed a relatively slow degenerate isomerization. After 32 h an equilibrium between **1**-d and **1'**-d was established, and according to mass spectrometric analysis of the mixture the original isotopic composition was unchanged.

Phototransformations of Compounds 1, 2, 3, and 5. – *Direct Irradiations.* When compound **1** was irradiated in benzene or acetonitrile with UV. light of >3400 Å, which is not absorbed by the photoisomers **2** and **3** (see Fig. 1 for the absorption spectra), only products **2** and **3** were formed in a 94:6 ratio (Table 1: no. 1 and 2)[4]. This ratio was independent of the extent of conversion of starting material, and of the extent of partial quenching with 0.1–0.8 M naphthalene (Table 2). Furthermore, a *Stern-Volmer* plot for the formation of **2** was linear in the concentration range of 0.0–0.1 M naphthalene (Fig. 2)[5].

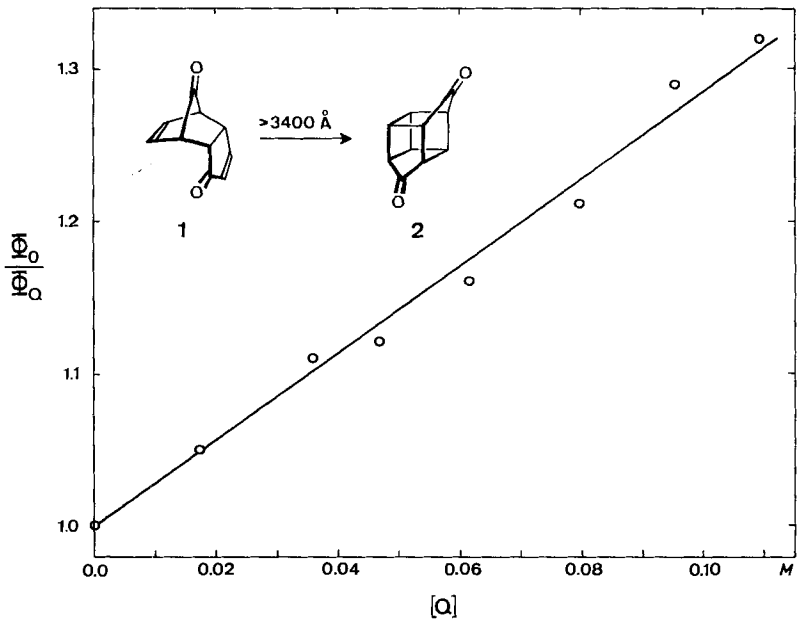


Figure 2. Stern-Volmer *plot: quenching of cage diketone* **2** *formation by naphthalene* UV. irradiation of $2.5 \cdot 10^{-2}$ M **1** in benzene at > 3400 Å

When the photolyses of **1** in benzene were carried out at > 3050 Å, where light absorption by **2** is appreciable, product **3** increasingly accumulated at the expense of **2** with increasing conversion of starting material (Table 1: no. 3), which suggested the existence of a photochemical equilibrium **1** ⇆ **2**. The photolytic reversal of the

[4] The photolyses of compounds **1**, **2**, **3**, and **5** also furnished small amounts of material of higher molecular mass [3] which was discarded. Quantitative product analyses were carried out with the crude reaction mixtures either by NMR. or by VPC. after catalytic hydrogenation which gave the tetrahydro derivatives of **1**, **3**, and **5** (= **11**) (compounds **1**, **3**, and **5** are unstable under VPC. conditions).

[5] Analysis by NMR.; the amounts of **3** formed in this experiment (maximum conversion of **1** ca. 25%) were insufficient for accurate measurements.

Table 1. *Examples of Direct and Sensitized Irradiations of Compounds* **1**, **2**, **3**, *and* **5**

Exper. no.	Compound	Sensitizer[a]	Solvent	Wavelengths	Product mixture[b] 1	2	3
1[c]	**1**	–	C_6H_6	>3400 Å	–	94%	6%
2[c]	**1**	–	CH_3CN	>3400 Å	–	94%	6%
3[d]	**1**	–	C_6H_6	>3050 Å	–	–	>90%
4[c]	**1**	acetophenone[c]	C_6H_6	>3050 Å	–	96%	4%[i]
5[d]	**1**	carbazole[f]	C_6H_6	>3400 Å	–	~95%	~5%
6[c]	**1**	carbazole	CH_3CN	>3050 Å	73%	25%	2%[i]
7[d]	**1**	benzophenone[g]	C_6H_6	>3050 Å	–	–	–
8[d]	**1**	thioxanthone[h]	C_6H_6	>3050 Å	~100%	–	–
9[d]	**2**	–	C_6H_6	>3050 Å	29%	56%	15%[i]
10[c]	**2**	acetophenone	C_6H_6	>3050 Å	–	~100%	–
11[d]	**3**	–	CH_3CN	2537 Å	17%	59%	24%[i]
12[d]	**3**	acetophenone	C_6H_6	>3050 Å	~25%	~45%	~30%[i]
13[d]	**3**	carbazole	CH_3CN	>3050 Å	–	–	100%
14[c]	**5**	–	C_6H_6	>3400 Å	–	35%	65%
15[c]	**5**	–	CH_3CN	>3400 Å	23%	35%	42%[i]
16[c]	**5**	acetophenone	C_6H_6	>3050 Å	–	94%	6%[i]
17[c]	**5**	carbazole	CH_3CN	>3050 Å	44%	10%	46%[i]

[a] $\gtrsim 98\%$ Absorption of incident UV. light by sensitizer. – [b] Compound **5** was not found as a component in the product mixtures of experiments 1–17. – [c] Product analysis by VPC. of the hydrogenated mixture (*cf.* footnote 4). – [d] Product analysis by NMR. – [e] E_T 72.0 kcal/mole [5]. – [f] E_T 70.1 kcal/mole [6]. – [g] E_T 67.6 kcal/mole [5]. Compound **1** was rapidly converted into a mixture of products other than **1**–**3** and **5**. – [h] E_T 65.5 kcal/mole [6]. – [i] Irradiation interrupted before photostationary state was reached.

Table 2. *Irradiation of Compound* **1**[a]: *Independence of Product Ratio* **2**/**3** *of Concentration of Added Naphthalene*

Concentration of naphthalene	0.0	0.1 M	0.2 M	0.4 M	0.6 M	0.8 M
Product ratio **2**:**3**[b] (in %)	95/5	94/6	95/5	96/4	95/5	96.5/3.5

[a] Benzene solution, >3400 Å. – [b] Analysis by NMR.; ±2%.

Table 3. *Irradiation of Compound* **2**[a]: *Independence of the Conversion* **2** + hν → **1** *of Concentration of Added 1,3-Pentadiene by* Stern-Volmer *Analysis*

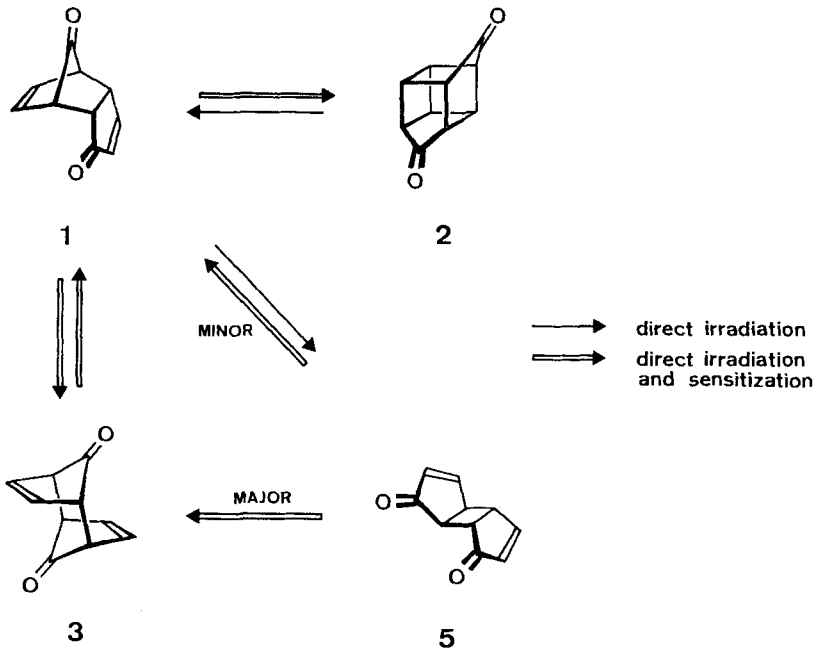
Concentration of 1,3-pentadiene	0.0	0.25 M	0.5 M	1.0 M	1.5 M	2.0 M	2.5 M	3.0 M
$\Phi_Q:\Phi_O$[b]	1.0	0.98	0.95	1.04	1.09	0.98	1.12	1.09

[a] Benzene solution, 3130 Å. – [b] Quantum yields (Φ) of conversion of **2**.

cycloaddition was confirmed by irradiation of **2** at > 3050 Å in benzene which afforded **1** and **3** (Table 1: no. 9). Addition of 1,3-pentadiene in concentrations up to 1 M did not quench the reaction of **2** (Table 3).

Compound **3** remained essentially unchanged at 3130 Å, but gave **1** and **2** at 2537 Å in acetonitrile solution (Table 1: no. 11) and the photolysis of compound **5** in benzene and acetonitrile at > 3400 Å afforded **1**, **2**, and **3** (no. 14 and 15). The reaction of **5** to **1** and **3** could not be quenched using up to 1.0 M naphthalene and 3.0 M 1,3-cyclohexadiene.

Scheme 3. *Photochemical Transformations of Compounds* **1**, **2**, **3**, *and* **5**[6])



A comparison of the rates of conversion of **1** and **5** in benzene under conditions (> 3400 Å) which provided for essentially monochromatic absorption by both compounds of the 3660 Å emission of the lamp, showed that **5** reacts ca. 8,5 times more rapidly than **1**. Although isomer **5** was not observable among the photoproducts of **1**, **2**, and **3**, evidence for its photochemical formation from **1** could be established by irradiation of a mixture of two parts of partially deuteriated **1** (**1**-d: 14% d_0, 33% d_1, 33% d_2, 16% d_3, 4% d_4) and one part **5** in benzene at > 3400 Å. The photolysis was interrupted before **5** was entirely consumed. Recovery of this compound and mass spectrometric analysis revealed a total deuteriation of 1–2% (**5**-d) and a deuterium distribution (d_1:d_2:d_3) which was similar to that of the starting **1**-d within the accuracy of mass spectrometric determination[3]).

[6]) The formation of cage diketone **2** on photolyses of compounds **3** and **5** is assumed to involve isomer **1** as an intermediate in each case and thus to represent the result of a two-step photochemical sequence.

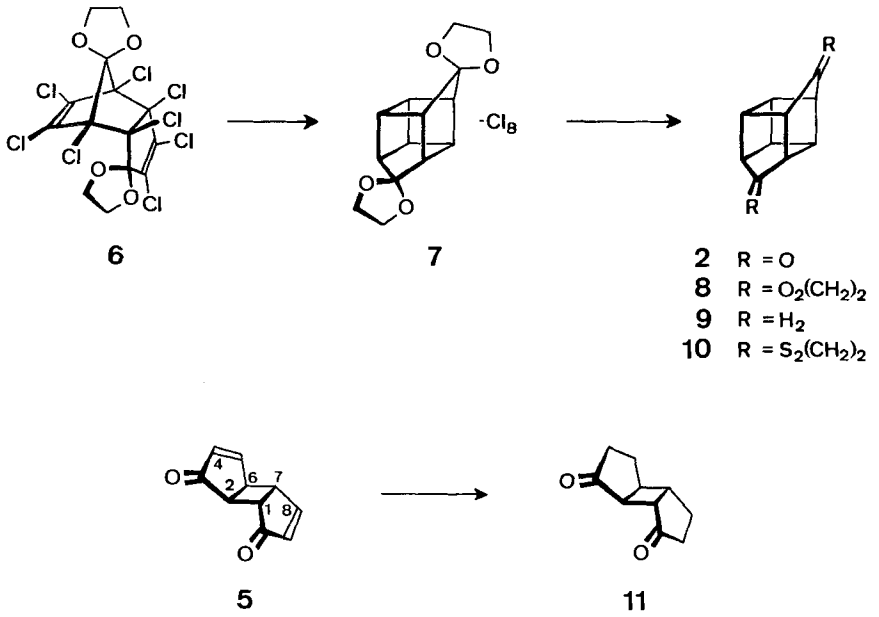
When the unsymmetrically deuteriated compounds **3**-d and **5**-d (for the preparation see «Thermal Transformations») were irradiated at 2537 and > 3400 Å, respectively, the mass spectrometric analysis of the products showed that the original isotopic composition in **1**-d, **2**-d, and **3**-d was fully retained in each case[3]).

Sensitization Experiments. The triplet-sensitized cycloaddition **1** → **2** with acetophenone in ethanol has been reported previously [3]. Table 1 summarizes the results of sensitized irradiations of compounds **1**, **2**, **3**, and **5** using various triplet sensitizers. We note in particular that the reaction **2** → **1** could not be sensitized with acetophenone, that carbazole sensitized the rearrangements **1** → **3** and **5** → **3** whereas sensitizers of lower triplet energy proved ineffective, and that the rearrangement **3** → **1** was achieved only with the higher energy sensitizer acetophenone[7]).

Structure Proof for Products 2 and 5. – Structure **2** had been assigned [3] to the cage diketone in analogy to photocycloadditions similar to **1** → **2**. Furthermore, the NMR. data of **2** (two-proton signals at δ 2.76 and 2.86, and a four-proton signal at δ 3.4) excluded the two symmetric structural isomers, pentacyclo[5.3.0.$0^{2,6}$.$0^{3,10}$.$0^{5,8}$]-decane-4,9-dione[8]) and the as yet unknown pentacyclo[5.2.1.$0^{2,6}$.$0^{3,9}$.$0^{5,8}$]decane-4,10-dione.

Chemical support for structure **2** has now been established by the following two correlations. The perchloro-diketal **6** [8] was subjected to acetophenone-sensitized

Scheme 4



[7]) The various sensitizers used (*cf.* Table 1) place the minimum triplet energies required for sensitization at ca. 68–70 kcal/mole for **1**, and **5**, and ca. 70–72 kcal/mole for **3**, assuming exothermic diffusion-controlled energy transfer mechanisms.

[8]) Reference to the preparation of this compound has recently been made by *Eaton* [7].

photocycloaddition. Reductive dechlorination of the octachloro cage product **7**, which was obtained in 75% yield, with sodium in *t*-butyl alcohol and tetrahydrofuran afforded 19% of the diketal **8**. This latter compound could also be prepared by ketalization of the photoproduct **2**. Alternately, *Huang-Minlon* reduction of **2** gave 37% of the known bishomocubane **9** [9]. An attempt to reduce diketone **2** by treatment of the dithioketal **10** with *Raney* nickel failed to yield the $C_{10}H_{12}$ hydrocarbon.

Catalytic hydrogenation of the di-enone **5** (IR.: $\nu_{C=C, C=O}$ = 1579, 1700 (shoulder), 1718 cm^{-1}; NMR.: δ 2.72/*d*, H–C(1) and H–C(2); 3.36/*bm*, H–C(6) and H–C(7); 6.43/*d*, H–C(4) and H–C(9); 7.81/*dd*, H–C(5) and H–C(8); $J_{1,7}/_{2,6}$ = 4 Hz, $J_{4,5}/_{8,9}$ = 5.5 Hz, $J_{5,6}/_{7,8}$ = 3 Hz) afforded the saturated diketone **11** which was identified with an authentic sample obtained by photodimerization of cyclopent-2-enone [10].

Discussion. – The observed photochemical transformations of the compounds **1**, **2**, **3**, and **5**, as summarized in Scheme 3[6]), do not necessarily account for all interconversions of these isomers which may occur under the reaction conditions employed. Compound **5** proved particularly elusive as a photoproduct, and its formation from **1** could only be detected when a mixture of deuteriated **1** and non-labeled **5** was photolyzed. This analytical difficulty is due to the considerably greater quantum yield of conversion of **5** relative to **1** and **3**, together with the greater absorbance of **5** in the $n \rightarrow \pi^*$ (*cf.* Fig. 1) and $\pi \rightarrow \pi^*$ regions. It is possible, therefore, that the «missing» transformations **1** → **5** (sensitized), and **1** ⇄ **1'** and **3** → **5** (direct and sensitized irradiations) are in fact operating but have escaped detection. The photorearrangement **5** → **3** has been established, furthermore, on the basis that the product ratios (**1** + **2**):**3** on direct excitation of **5** at > 3400 Å in benzene and acetonitrile (Table 1: no. 14 and 15) are quite different from the **2**:**3** ratios in the corresponding photolyses of **1** (Table 1: no. 1 and 2). These differences are clearly too large to allow for the secondary rearrangement **1** → **3** as the only route to **3** in runs 14 and 15, and thus establish the additional direct conversion **5** → **3**.

The results of the triplet quenching and sensitization studies with compound **1** under conditions which do not change products **2** and **3** (*i.e.*, irradiation at >3400 Å and sensitization with carbazole), indicate that triplet pathways are followed also on singlet excitation of this compound. The evidence rests in particular on the linearity of the *Stern-Volmer* plots obtained on quenching of **1** (*cf.* Fig. 2 and Table 2) and on the formation of similar values for **2**:**3** on selective singlet excitation and triplet sensitization of **1** (Table 1: no. 1, 2, 5, and 6)[9]).

The informations concerning the multiplicity of the remaining reactions are incomplete. The sensitizations of **3** and **5** (Table 1: no. 12, 13, 16, and 17) establish that the triplet excited states of these ketones can rearrange. The multiplicity of the reactions **1** → **5** and **3** → **1** on singlet excitation remains unexplored, however, and the

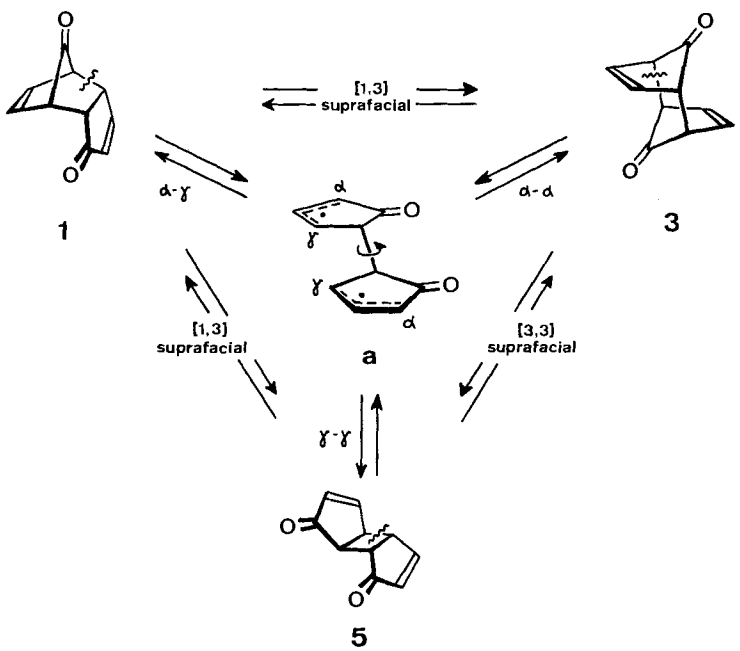
[9]) This argument is valid barring the unlikely coincidence that the singlet and triplet excited states of **1** possess the same specific reactivities leading to products **2** and **3** *via* at least two obviously different mechanistic paths (it is reasonably assumed that the primary photochemical process of the [2+2] cycloaddition **1** → **2** is not identical with that of any of the rearrangements). A similar argument based on the invariance of the product ratio (**1**+**2**):**3** formed on singlet excitation and triplet sensitization of **5** (Table 1: no. 15 and 17) is applicable only if products **1** and **3** do not derive from **5** *via* a common ground state intermediate such as **a** (*cf.* Scheme 5).

lack of any quenching effect by 3 M 1,3-pentadiene on **2** → **1** and by 1 M naphthalene and 3 M 1,3-cyclohexadiene on **5** → **1** + **3** indicates only that the reactive species of **2** and **5**[10]) are not amenable to diffusion-controlled triplet quenching.

We established in our earlier work [3] that the dominant path for **1** $\xrightarrow{h\nu}$ **3** is an intramolecular rearrangement. The intramolecular nature of the thermal and photochemical isomerizations **3** → **1** and **5** → **1** has now been demonstrated as well in the corresponding experiments with compounds **3**-d and **5**-d. These results exclude the possibility that **3** and/or **5** undergo two bond cleavages to cyclopentadienone[11]) followed by thermal *Diels-Alder* dimerization to **1**. Furthermore, similar findings have been established for the thermal interconversion **1** ⇄ **1'**.

The photochemical conversions **1** ⇄ **3** and **1** ⇄ **5** are formal examples of allowed [1, 3] suprafacial sigmatropic rearrangements (*cf.* Scheme 5), and the thermal conversion **1** ⇄ **1'** corresponds to an allowed [3, 3] suprafacial *Cope* type process [15] which is frequently encountered in such systems (*e.g.*, **15** → **16** [16]). On the other hand, the thermal isomerizations **3** → **1** + **5** and **5** → **1** and the photoreaction **5** → **3** are forbidden

Scheme 5[12])



[10]) Triplet reactivity of **5** on direct excitation is likely, however, in view of the efficient intersystem crossing of cyclopenten-2-one [11] and its derivatives (particularly such with rigid conformations [12]). The triplet nature of the reaction **1** → **5** appears probable for the same reason.

[11]) *cis,anti,cis*-Tricyclo[5.2.0.0^{2,6}]deca-3,9-diene [13] and 6,7-dimethyl-*cis,ξ,cis*-tricyclo-[5.3.0.0^{2,6}]deca-3,10-dione [14] photochemically revert to the monomers, cyclopentadiene and 3-methylcyclopent-2-enone, respectively.

[12]) The notations [1,3] *suprafacial* and [3,3] *suprafacial* refer to the respective overall structural changes and are not meant necessarily to infer concertedness of the rearrangement mechanisms.

by orbital symmetry conservation rules, and therefore are most likely a priori to be nonconcerted rearrangements. These nonconcerted interconversions of the compounds **1**, **3**, and **5** involve the cleavage of a bond, as marked in Scheme 5 for each diketone, which is properly aligned in each case with the allylic π-systems at both sides to facilitate this process, followed by internal reorganization of the diradical intermediate **a** (α-α bonding $\rightarrow$ **3**, α-γ $\rightarrow$ **1**, γ-γ $\rightarrow$ **5**)[13].

The slow thermal *Cope* type isomerization **1** $\rightleftharpoons$ **1'** is not accompanied by any other rearrangement involving nonconcerted paths to **3** and **5**. It is likely, therefore, that **1** $\rightleftharpoons$ **1'** is indeed concerted rather than proceeding via an intermediate common to the thermal conversions of **3** and **5**. On the other hand, the photoisomerization of **5** in benzene prefers the nonconcerted path to **3** over the formally allowed concerted rearrangement to **1**, and in acetonitrile the predominance of the latter is only marginal (Table 1: no. 14, 15, and 17). For this reason, the question remains whether concerted mechanisms are followed at all in the triplet photorearrangements, the possibility existing that they also rather proceed along two-step paths *via* the common intermediate **a** (it is assumed that the photogenerated triplet diradical would undergo spin inversion prior to recombination and thus would become identical with the singlet diradical intermediate proposed for the thermal reactions of **3** and **5**)[14].

Supplementary results to the photorearrangement **5** $\rightarrow$ **1** can be found in the conversions **12** $\rightarrow$ **1** [13] and **13** $\rightarrow$ **14** [7] (Scheme 6) as reported by *Eaton et al.* The former reaction has been shown experimentally to be an intramolecular rearrangement (as must be the latter). Evidently it is not reversible. The transformation **12** $\rightarrow$ **1** involves a bond cleavage between C(1) and C(2), while the reverse reaction (**1** $\rightarrow$ **12**) would require a less favorable cleavage between C(1) and C(2) as compared to the preferred cleavage of the doubly allylic bond between C(6) and C(7) which actually occurs in the process **1** $\rightarrow$ **3** + **5**. These results along with other most recent ones on substituted compounds [2] [20–23] constitute further examples of interconversions of cyclopentadienone dimers to those described in this work.

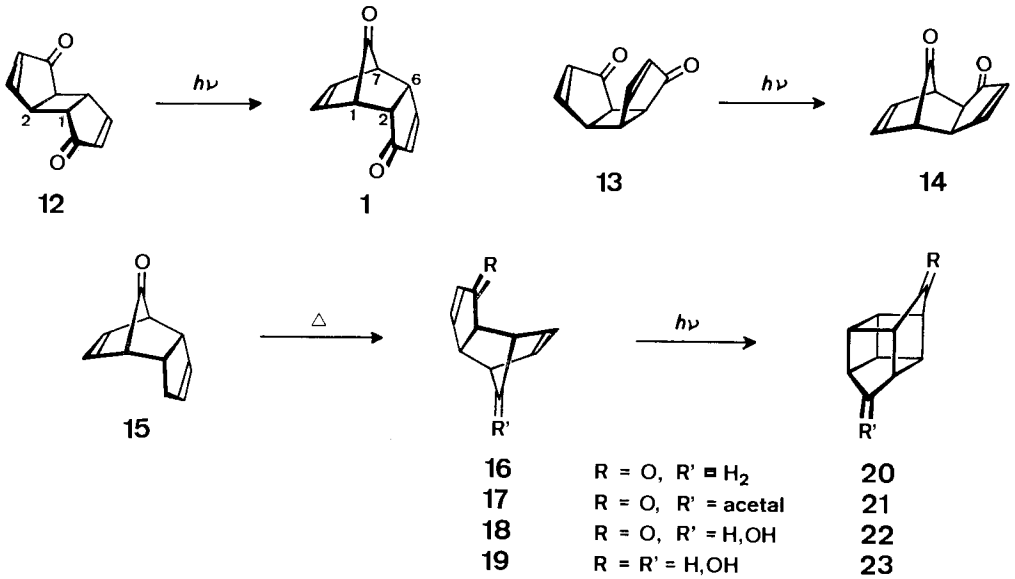
The cycloaddition **1** $\rightarrow$ **2** and the rearrangement **1** $\rightarrow$ **3** have been shown to occur from the same triplet excited state to the extent that no differential quenching of the two processes could be achieved (*vide supra*). Although the spectral characteristics of **1** (norbornen-7-one [16a] and cyclopentenone partial structures; *cf.* Fig. 1) ensure that the α,β-unsaturated ketone is the site of primary excitation on direct irradiation at > 3400 Å, the definite assignment of the reacting triplet excited state is not possible at present. Internal photochemical [2 + 2] cycloadditions in the *endo*-dicyclopentadiene

[13] Such a two-step mechanism *via* the diradical **a** has already previously been considered for **1** + $h\nu$ $\rightarrow$ **3** [3] (an intermediate of type **a** has been discussed by *Woodward & Katz* [16a] for the rearrangement of *endo*-dicyclopentadienes). – Attempts to trap **a** by radical scavengers have failed so far; *e.g.*, addition of 0.65 M 2,2,6,6-tetramethylpiperidine oxide [17] to 0.63 M **1** in benzene did not effect any quenching of the transformation to **3** at >3400 Å, and no adducts with the N-oxide were formed. A similar negative result was obtained with the N-oxide and **5** in acetonitrile.

[14] A formal example of an allowed [1,3] suprafacial sigmatropic photorearrangement has been established to be nonconcerted by *Cargill et al.* [18]. *Scheffer et al.* [19] recently reported on thermal and photochemical isomerizations of an $\alpha,\beta;\delta,\varepsilon$-bis-unsaturated γ-hydroxyketone which include formal [1,3] and [3,3] suprafacial sigmatropic rearrangements and represent some analogy to the present cases concerning the mechanistic implications.

system do not necessarily require any of the two keto groups present in **1**, whereas both the bridge carbonyl and the isolated double bond are *conditio sine qua non* for rearrangements of type **1** → **3**. The following observations illustrate this point:

Scheme 6



1) Cage products have also been prepared either by direct irradiation of compounds lacking the bridge carbonyl (**16** → **20** [16a], **17** → **21** [24] [25], *substituted*-**18** → *substituted*-**22** [20]) or by sensitization of compounds lacking both carbonyls (**6** → **7**, *endo*-dicyclopentadiene → **9** [9]; **19** → **23** [16a]).

2) Rearrangements of type **1** → **3** neither occur with any of the above cited *endo*-tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene derivatives nor with 8,9-dihydro-**1** (*endo*-tricyclo[5.2.1.$0^{2,6}$]deca-4-ene-3,10-dione) [25].

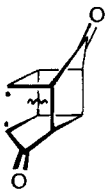
It appears premature to distinguish between several possibilities to explain the required presence of both the bridge carbonyl and the isolated double bond for the rearrangement. The two groups may provide for better stabilization of the incipient diradical (**a**) and thus critically facilitate the bondbreaking process when initiated in the triplet excited state of the α,β-conjugated ketone. Moreover, there is the possibility of intramolecular triplet energy transfer from the α,β-unsaturated to the β,γ-unsaturated carbonyl system. This transfer appears feasible energetically but cannot be distinguished from a reaction of the triplet cyclopentenone on energetic grounds alone in view of the relatively narrow range of the triplet energies of cyclopent-2-enones [11] [12] [26] and β,γ-unsaturated ketones [27][15]) around 70 kcal/mole.

The photochemical conversion of cage diketone **2** to **1** deserves some comment, particularly since this behavior is duplicated by a variety of substituted analogs of **2** [21] [22]. It is likely that the reaction is initiated by photolytic cleavage of one of

[15]) We thank Professor *K. G. Hancock* for communicating his results on the energy and nature of the triplet state in β,γ-unsaturated ketones prior to publication.

the cyclobutane bonds α to a keto group, followed by further cleavage of the resulting 1,4-diradical **b**. Both the geometry of the breaking σ bond relative to the carbonyl π system and its considerable strain may favor this 'π*-assisted' photocleavage. Precedence for this reaction may be found in many examples of the photochemical reversal of [2 + 2] cycloaddition, notably in dimers of pyrimidines such as thymine[16]) and of conjugated ketones. A particularly close analogy presents itself in the photochemical cleavage of the head-to-tail dimer of 3-methylcyclopent-2-enone [14][11]) which presumably leads to an intermediate that – similar to **b** – is stabilized only by one adjacent keto group.

Scheme 7



b

We gratefully acknowledge financial support for this research afforded by the *Schweiz. Nationalfonds zur Förderung der wissenschaftlichen Forschung* (projects no. 2.146.69 and 2.505.71), *CIBA-GEIGY AG*, Basel, and *Firmenich & Cie*, Geneva (to *U. K.*, *J. G.*, and *K. S.*). *J. G.* thanks for a *National Research Council Scholarship of Canada*.

Experimental Part

General Remarks. UV.-Irradiations were carried out at room temperature using 125 W medium-pressure (QM 125, *Meda Licht AG*, Basel) and low-pressure Hg lamps (NK 6/20, *Quarzlampen GmbH*, Hanau) in central water-cooled Pyrex and quartz fingers, respectively. When filter solutions were employed, these were placed in an additional jacket of 1 cm inner width which surrounded the Pyrex finger (cut-off at ~3050 Å: aqueous 0.1 M KH-phthalate solution; ~3400 Å: aqueous solution of 750 g NaBr + 8 g $Pb(NO_3)_2$ per liter). For preparative experiments the finger was immersed into the center of the diketone solution, while runs on analytical scale were carried out in 10 ml Pyrex and quartz tubes, respectively, which were placed next to the finger. The reaction solutions were magnetically stirred during the irradiation. – Gas chromatograms (VPC.) were run on *Perkin-Elmer* 990 chromatographs on a column packed with 5% SE-30 on chromosorb G-AW-DMCS (80–100 mesh) at 150–220°. Integrations of peak areas of tetrahydro-**1**, **2**, tetrahydro-**3**, and **11** were calibrated with standard solutions of these compounds. – For thin-layer chromatograms (TLC.) *Merck* Fertigplatten F_{254} (silica gel) were used. The spots were located by fluorescence (irradiation at 2537 Å) and either by treatment with conc. H_2SO_4 (compounds **1–3**) or with J_2 vapor (compound **5**). – M.p. (taken in open capillaries in an oil bath) are not corrected. – UV. spectra: λ_{max} in nm, ε values in parentheses. – IR. spectra: ν_{max} in cm^{-1}. – NMR. spectra: Chemical shifts in δ values, with $(CH_3)_4Si$ as internal standard. Abbreviations: *s* (singlet), *d* (doublet), *m* (multiplet), *b* (broad), and *J* (coupling constant in Hz). Proton integration of each signal is in agreement with the assignments given.

Thermal Transformations. – endo-*Tricyclo[5.2.1.0^{2,6}]deca-4,8-diene-3,10-dione* (**1**). A ca. 5% solution of **1** in hexachlorobutadiene containing octamethylcyclotetrasiloxane as internal standard was heated from 22° to 140° in the NMR. (60 MHz) probe and its spectrum was measured at intervals. No change occurred until at 120° **1** began to decarbonylate to **4**.

25 mg **1**-d (MS.: 14% d_0, 33% d_1, 33% d_2, 16% d_3, 4% d_4) in 2 ml hexachlorobutadiene were heated to 90° for 32 h. The product analysis was performed by integration of the NMR. proton

16) For leading references see [29].

signals at 100 MHz. No signals attributable to **3** and **5** had appeared after the thermal treatment. The percentages of the total proton intensity (0 h/32 h) were 30/27 for H—C(1,7), 12/13 for H—C(2), 38/38 for H—C(4, 8, 9), 17/14 for H—C(5), and 3/8 for H—C(6). Furthermore, the intensity of the two peripheral lines of the four-line spectrum of H—C(5) in **1**-d, which initially were ca. $^1/_5$th of the two central lines, had increased by ca. 100% after the heating.

anti-*Tricyclo*[*4.2.1.1*^{2,5}]*deca-3,7-diene-9,10-dione* (**3**). a) A solution of 50 mg **3** in 3 ml CCl_4 was refluxed for 8 h under argon. The product composition was directly determined by NMR. (60 MHz): 61% **1**, 9% **3**, 30% **5**.

b) A solution of 300 mg **3** in 3 ml hexachlorobutadiene was heated to 140° for 15 min under argon. On cooling cis,anti,cis-*tricyclo*[*5.3.0.0*^{2,6}]*deca-4,8-diene-3,10-dione* (**5**) precipitated. The crystals were washed with hexane, crystallized from $CHCl_3$-hexane, and sublimed at 120°/0,001 Torr to give 15 mg of m.p. 175–176°. UV. (C_2H_5OH): ca. 235 (shoulder), 216 (15700); 324.5 and 335 (193; broad); (C_6H_6): see Fig. 1. IR. ($CHCl_3$): 829, 1084, 1343, 1579, ca. 1700 (shoulder), 1718. NMR. (100 MHz, $CDCl_3$): 2.72/*d*, $J_{1,7/2,6}$ = 4, H—C(1) and —C(2); 3.36/*bm*, H—C(1) and —C(7); 6.43/*d*, $J_{4,5/8,9}$ = 5.5, H—C(4) and —C(9); 7.81/*dd*, $J_{5,6/7,8}$ = 3, $J_{4,5/8,9}$ = 5.5, H—C(5) and —C(8). MS.: 160 (M^+), 132, 131, 109, 108, 78, 51, 44, 28 (base peak).

$C_{10}H_8O_2$ Calc. C 74.99 H 5.03% Found C 74.82 H 4.93%

c) A solution of 100 mg **3**-d [4% d_0, 20% d_1, 37% d_2, 29% d_3, 10% d_4; prepared by deuteriation of **1** with PCl_5/D_2O and photorearrangement of product **1**-d (*cf.* [3])] in 1.5 ml hexachlorobutadiene was heated for 7 min to 140°. After cooling the precipitate was filtered off, washed with hexane, dissolved in CH_2Cl_2 and filtered through neutral Al_2O_3 (act. III). Subsequent chromatography on 2 g silical gel *Merck* (mesh 0.02–0.5 mm) with benzene/ethyl acetate 1:1 gave 2 mg **1**-d and 17 mg **5**-d. MS.: the isotopic composition of the two products was identical with that of the starting material (**3**-d)[3][17]).

cis,anti,cis-*Tricyclo*[*5.3.0.0*^{2,6}]*deca-4,8-diene-3,10-dione* (**5**). a) A solution of 5 mg **5** in 0.5 ml $CHCl_3$ was heated in a sealed tube to 150° for 30 min. The solvent was evaporated, and the residue was hydrogenated on 10 mg 10% Pd/$BaSO_4$ in 2 ml CH_3OH. Only tetrahydro-**1** and **11** could be detected by VPC. in the residue after removal of the catalyst and solvent. VPC. screening for tetrahydro-**3** [3] was negative.

b) A solution of 22 mg **5**-d (*vide supra* for the preparation) in 1 ml hexachlorobutadiene was heated for 30 min to 180°, then diluted with acetone and filtered. A sample of **4**-d was isolated by preparative VPC. MS.: isotopic composition identical with that of starting material (**5**-d)[3][17]).

Photochemical Transformations. – endo-*Tricyclo*[*5.2.1.0*^{2,6}]*deca-4,8-diene-3,10-dione* (**1**). a) Two solutions of 50 mg **1** each in 10 ml CH_3CN and benzene, respectively, were photolyzed at >3400 Å for 3 h. The solvents were evaporated *in vacuo*, and the residues were hydrogenated on 20 mg 10% Pd/$BaSO_4$ in 3 ml CH_3OH. VPC.: Table 1, no 1 and 2.

b) A solution of 55 mg **1** in 10 ml benzene was irradiated at >3050 Å for 16 h. After removal of the precipitate by filtration, the filtrate was taken to dryness. NMR. (60 MHz, $CDCl_3$) analysis of the crystalline residue (45 mg): Table 1, no 3.

c) A solution of 40 mg **1**-d (MS.: 14% d_0, 33% d_1, 33% d_2, 16% d_3, 4% d_4; obtained on deuteriation of **1** with PCl_5/D_2O as previously described [3]) and 20 mg **5** in 5 ml benzene was photolyzed at >3400 Å for 7.5 min. After evaporation of the solvent, the residue was chromatographed on a column of 8 g silical gel *Merck* (0.05–0.2 mm). Elution with benzene/ethyl acetate 1:1 gave 8 mg **5** which exhibited a total deuteriation of ca. 1–2% (**5**-d) and a deuterium distribution (d_1:d_2:d_3) which was similar to that of starting **1**-d within the accuracy of mass spectrometric determination.

A control run in which a similar solution of **1**-d and **5** was analogously processed *without* UV. irradiation, the recovered sample of **5** contained no deuterium[3][17]).

d) 20 mg **1** in 10 ml benzene ($1.3 \cdot 10^{-2}$ M) were subjected to sensitized irradiation at >3050 Å for 3 h using 2.0 g acetophenone (1.67 M). The mixture was taken to dryness in vacuo and hydrogenated in 3 ml CH_3OH on 20 mg 10% Pd/$BaSO_4$. VPC.: Table 1, no 4.

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[17]) The isotopic compositions of products **1**-d, **2**-d, **3**-d, **4**-d, and **5**-d were determined by measurement of the predominant MS. peak groups 132–136 and 104–108 (M^+ and $M^+ - CO$, respectively, for **4**-d, and $M^+ - CO$ and $M^+ - 2CO$, respectively, for **1**-d, **2**-d, **3**-d, and **5**-d).

e) 50 mg **1** in 100 ml benzene ($\sim 3.1 \cdot 10^{-3}$ M) were subjected to sensitized irradiation at >3400 Å for 4 h using 650 mg carbazole ($\sim 38.9 \cdot 10^{-3}$ M). After the removal of a few mg precipitate, the solvent was evaporated. The residue was taken up in cold $CHCl_3$, and the largely insoluble sensitizer was removed by filtration. Concentration of the filtrate in vacuo and chromatography of the residue on a column of 30 g silica gel *Merck* (0.05–0.2 mm) with hexane/ether 1:1 gave a product mixture which was analyzed by NMR. (60 MHz; $CDCl_3$): Table 1, no. 5; a relatively large error in the integration was due to the presence of small amounts of impurities.

Irradiation of 15 mg **1** ($\sim 9.4 \cdot 10^{-3}$ M) and 130 mg carbazole ($\sim 7.8 \cdot 10^{-2}$ M) in 10 ml CH_3CN at >3050 Å for 2 h was followed by evaporation *in vacuo* and hydrogenation of the residue on 20 mg 10% $Pd/BaSO_4$ in 3 ml CH_3OH. VPC.: Table **1**, no. 6.

f) A mixture of 45 mg **1** (~ 0.028 M) and 81 mg benzophenone (~ 0.044 M) in 10 ml benzene was irradiated at >3050 Å for 5 h to give a yellow oil in which none of the products **1**–**3** and **5** could be detected by TLC. and NMR. (60 MHz; $CDCl_3$). In a similar experiment using thioxanthone **1** could be recovered almost quantitatively (Table **1**: no. 7 and 8).

g) A series of 5 ml benzene solutions of ~ 0.062 M **1** and 0.0–0.8 M naphthalene were photolyzed at >3400 Å for 15 h in a turn-table reactor. The insoluble material formed in each sample was removed by filtration, and the quencher was separated by column chromatography on 30 g silica gel *Merck* (0.05–0.2 mm) with hexane-ether in each case. The **2**:**3** ratio in the eluted mixtures of **1**–**3** (ca. 35 mg) was determined by NMR. (60 MHz; $CDCl_3$): see Table 2 for results.

h) A series of 5 ml benzene solutions of ~ 0.025 M **1** and 0.0–0.11 M naphthalene were irradiated at >3270 Å (acetone as filter) for 30 min in a turn-table reactor. At a ca. 25% conversion of **1** in the naphthalene-free sample the reaction was stopped, the precipitate filtered off and the solvent evaporated. The formation of **2** was determined by NMR. (60 MHz; $CDCl_3$): see *Stern-Volmer* plot, Fig. 2, for the results.

Pentacyclo[5.3.0.0^{2,6}.0^{4,10}.0^{5,8}]decane-3,9-dione (**2**). a) A solution of 35 mg **2** in 10 ml benzene was irradiated at >3050 Å for 21 h. NMR. (60 MHz; $CDCl_3$) analysis of the reaction mixture after evaporation of the solvent gave ca. 10% **2** and 90% **3**.

For the results of a similar run which was conducted to only 50% conversion of **2**, see Table 1, no. 9.

b) Irradiation of 10 mg **2** ($\sim 6.3 \cdot 10^{-3}$ M) and 2.0 g acetophenone (~ 1.67 M) in 10 ml benzene at >3050 Å for 3 h was followed by evaporation *in vacuo* and treatment of the residue with H_2 in the presence of 20 mg 10% $Pd/BaSO_4$ in 3 ml CH_3OH. VPC. analysis showed a quantitative recovery of **2** (Table 1, no. 10), whereas in a similar experiment *without* sensitizer the reaction mixture was composed of 29% tetrahydro-**1**, 56% **2**, and 15% tetrahydro-**3**.

c) A series of 5 ml benzene solutions of ~ 0.012 M **2** and 0.0–3.0 M 1,3-pentadiene were degassed (three freeze-pump-thaw cycles) in Pyrex tubes and photolyzed at 3130 Å (aqueous solution of 60 mg K_2CrO_4 and 17 mg KOH per liter) for 3 h in a turn-table reactor. At a ca. 30% conversion of **2** the reaction was stopped, and the solvent evaporated. The concentration of unreacted **2** was measured by VPC. in benzene solutions containing *n*-$C_{17}H_{36}$ as a standard: see Table 3 for the results.

anti-*Tricyclo[4.2.1.1^{2,5}]deca-3,7-diene-9,10-dione* (**3**). a) 34 mg **3** in 5 ml CH_3CN were photolyzed at 2537 Å for 39 h. NMR. analysis (60 MHz; $CDCl_3$) of the residue after evaporation of the solvent: Table 1, no 11.

b) Sensitized irradiation of 40 mg **3** in 3 ml benzene (~ 0.08 M) at >3050 Å for 11 h using 70 mg acetophenone (~ 0.175 M) was followed by evaporation of the solvent and NMR. (60 MHz; $CDCl_3$) analysis of the residue: Table **1**, no. 12.

c) On attempted sensitized irradiations of **3** + carbazole in CH_3CN at >3050 Å, **3** + benzophenone in benzene at >3050 Å, and **3** + thioxanthone in benzene at >3400 Å only starting material was quantitatively recovered (Table 1, no. 13).

d) 100 mg **3**-d (for preparation see 'Thermal Transformations') in 6 ml CH_3CN were photolyzed in a quartz tube for 3 h with the medium-pressure Hg lamp. The solution was filtered through neutral Al_2O_3 (act. III) and the filtrate was taken to dryness. Chromatography on 5 g silica gel *Merck* (0.02–0.5 mm) with benzene/ether 1:1 gave, *inter alia*, 15 mg **3**-d [NMR. (60 MHz; $CDCl_3$): ratio $H_{olef/sat} = 3$ as in starting material] and 10 mg **1**-d which were sublimated at 90°/0.01 Torr. MS.: identical deuterium distribution for starting material (**3**-d) and **1**-d^3)[17]).

cis, anti, cis-*Tricyclo[5.3.0.0^{2,6}]deca-4,8-diene-3,10-dione* (**5**). a) A solution of 10 mg **5** in 2 ml benzene was photolyzed at >3400 Å for 1.5 h. After evaporation of the solvent, the residue was dissolved in 5 ml CH_3OH and hydrogenated on 20 mg 10% $Pd/BaSO_4$. VPC.: Table 1, no. 14 (tetrahydro-**1** and **11** could not be found).

b) 15 mg **5** in 10 ml CH_3CN were irradiated at >3400 Å for 1.5 h and worked up as described above. VPC.: Table 1, no. 15.

c) 13.5 mg **5** (~0.0084 M) and 2.0 g acetophenone (~1.67 M) in 10 ml benzene were irradiated at 3050 Å for 3 h. The solvent was evaporated and the residue hydrogenated as described above. VPC.: Table 1, no. 16.

d) A solution of 15 mg **5** (~$9.4 \cdot 10^{-3}$ M) and 130 mg carbazole (~$7.8 \cdot 10^{-2}$ M) in 10 ml CH_3CN was photolyzed at >3050 Å for 1 h. The solvent was evaporated and the residue was hydrogenated as described above. VPC.: Table 1, no. 17.

e) Two pairs of 1-ml benzene solutions of 5 mg **5** each without and with ~1.0 M naphthalene, respectively, were simultaneously irradiated at >3400 Å for periods of 5 and 10 min. The solvent was evaporated and the residues were hydrogenated as described above. VPC.: the rates of conversion of **5** to **1** and **3** were not affected by naphthalene.

A similar series was carried out with 0.5 ml benzene solutions of 1 mg **5** each without and with ~3.0 M 1,3-cyclohexadiene. Again, no quenching was observed.

f) Two solutions of 16 mg **5**-d (for preparation see 'Thermal Transformations') in 3 ml benzene were irradiated at >3400 Å for 12 and 45 min, respectively. Chromatography on silica gel *Merck* (0.05–0.2 mm) gave 7 mg **3**-d from the first run (elution with benzene/ethyl acetate 1:1), and 4 mg **2**-d from the second experiment (elution with ether/hexane 9:1). MS.: the deuterium distribution in the starting material (**5**-d) and in both products were identical.

Photochemical Conversion of Compounds **1** *and* **5***: Quantum Yield Ratio.* Solutions of equal optical density at 3660 Å of compounds **1** and **5** in benzene (75 mg **1** and 25 mg **5** in 10 ml each) were photolyzed at >3400 Å in a turn-table reactor. Aliquots of 2 ml were removed periodically from each tube. The solvent was evaporated, and the residue hydrogenated on 20 mg 10% $Pd/BaSO_4$ in 3 ml CH_3OH. Each of the crude product mixtures was dissolved in 0.5 ml acetone containing 0.45% naphthalene as standard for VPC. analysis. Results: Table 4; $\Phi_{-5}/\Phi_{-1} \sim 8.5$.

Table 4. *Comparison of the Efficiency of Photochemical Conversion of* **1** *and* **5** *at >3400 Å*

Irradiation time	Concentration (standardized values) [**1**]	[**5**]
0 min	1.00	1.00
5 min	0.92	0.27
10 min	0.81	0
15 min	0.74	

Structure Proof for Pentacyclo[5.3.0.0^{2,6}.0^{4,10}.0^{5,8}] decane-3,9-dione (2) and *cis, anti, cis*-Tricyclo [5.3.0.0.^{2,6}] deca-4,8-diene-3,10-dione (5). – *1,2,4,5,6,7,8,10-Octachloropentacyclo[5.3.0.0^{2,6}.0^{4,10}.0^{5,8}]decane-3,9-dione Di(ethyleneketal)* (**7**). A solution of 1 g *endo*-1,2,4,5,6,7,8,9-octachlorotricyclo[5.2.1.0^{2,6}]deca-4,8-diene-3,10-dione di(ethyleneketal) (**6**) [8] and 5 g acetophenone in 50 ml dry benzene was purged with N_2 and irradiated in a *Rayonet* reactor with *Sylvania* F8T5 blackray lamps (350 nm) for 16 h. The solvent and sensitizer were removed *in vacuo*. Crystallization of the residue from CH_3OH gave 0.75 g **7**, m.p. 319°. IR. (KBr): 1180. NMR. (60 MHz; $CDCl_3$): 4.16–4.36/*m*, $(CH_2)_2O_2$–C(3) and –C(9).

$C_{14}H_8Cl_8O_4$ Calc. C 32,06 H 1.53 Cl 54.20% Found C 32,06 H 1.77 Cl 52.81%

Pentacyclo[5.3.0^{2,6}.0^{4,10}.0^{5,8}]decane-3,9-dione Di(ethyleneketal) (**8**). 4.44 g (0.192 g-atoms) Na were added to 3.2 g (0.6 mmole) **7** in 40 ml tetrahydrofuran and 6.91 g (96 mmole) *t*-butyl alcohol. The reaction mixture was stirred under N_2 for two days at 0° and for four days at room temperature. After removal of the residual Na the solution was poured onto ice. Extraction with ether and crystallization of the crude product from C_2H_5OH yielded 0.6 g **8**, m.p. 93–94.5°. IR. (KBr):

1200. NMR. (60 MHz; $CDCl_3$): 2.42–2.58 (4H)/*m*; 2.8–3.15 (4)/*m*; 3.84–4.02/*m*, $(CH_2)_2O_2$—C(3) and —C(9). $C_{14}H_{26}O_4$ Calc. C 67.74 H 6.45% Found C 68.08 H 6.66%

The compound **8** was identical with a sample prepared by ketalization of diketone **2** with ethylene glycol and *p*-toluenesulfonic acid in boiling benzene.

Pentacyclo[5.3.0.0^{2,6}.0^{4,10}.0^{5,8}]decane (**9**). A solution of 500 mg **2** and 1 ml $NH_2NH_2 \cdot H_2O$ in 20 ml triethylene glycol was stirred overnight at room temperature under N_2. 4 g KOH were then added and the temperature was gradually raised to 200°. After 2.5 h at this temperature under a slow stream of N_2, 150 mg of crystalline **9** had precipitated in the ice-cooled receiver (identification by comparison [mixed m.p., TLC., IR., NMR.] with an authentic sample prepared by irradiation of *endo*-dicyclopentadiene [9]).

Pentacyclo[5.3.0.0^{2,6}.0^{4,10}.0^{5,8}]decane-3,9-dione Di(ethylenethioketal) (**10**). 1 ml BF_3 etherate was added to a solution of 1 g **2** in 3 ml ethanedithiol. An exothermic reaction immediately took place and a precipitate was formed. After 5 min CH_3OH was added. Crystallization of the solid from CH_3OH gave 1.7 g **10**, m.p. 171–173°. IR. (KBr): 1410. NMR. (60 MHz; $CDCl_3$): 2.7–3.05 (8H)/*m*; 3.12–3.25/*m*, $(CH_2)_2S_2$—C(3) and —C(9).

$C_{14}H_{26}S_4$ Calc. C 53,82 H 5,13 S 41.02% Found C 53.87 H 5.26 S 40.82%

Raney-Ni desulfurization attempts of **10** to **9** were unsuccessful.

Hydrogenation of **5**. 16 mg **5** were hydrogenated in 3 ml CH_3OH on 20 mg 10% $Pd/BaSO_4$ catalyst. VPC. purification of the crude product gave 8 mg cis,anti,cis-*tricyclo[5.3.0.0^{2,6}]decane-3,10-dione* (**11**) (identification by comparison [mixed m.p., TLC., IR., NMR.] with an authentic sample prepared by irradiation of cyclopent-2-enone [10]).

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268. Eine Apparatur zur automatischen Bestimmung von Wasserdampf-Sorptions-Isothermen und -Isobaren

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Summary. An apparatus for the automatic determination of water vapor sorption isotherms and isobares is described. Its main parts are a Cahn electrobalance and a gas circulating system. The gas can be held at constant dew points between – 85 and + 25 degree by an ultracryostate and an ultrathermostate and brings the sorbens to hygroscopic equilibrium.

Im organisch-chemischen Institut der Universität Bern werden seit mehreren Jahren Wasserdampf-Sorptions-Messungen an verschiedenen Stoffen ausgeführt[1]). Diese Arbeiten, sowie das Literaturstudium zu einer Monographie über die «Methodik der Wasserdampf-Sorptionsmessungen»[2]), liessen die Wünschbarkeit und Realisierbarkeit einer automatischen Sorptionsapparatur erkennen, die folgenden Anforderungen entspricht:

1. dem heutigen Stand der Wägetechnik entsprechende maximale Genauigkeit bei möglichst kleinen Substanzmengen;

2. automatische Aufnahme von Sorptions- und Desorptionsisothermen in beliebigen Abständen der Wasseraktivität;

3. geschlossenes System, in welchem der Sorptionsvorgang nicht durch periodische Wägungen unterbrochen wird und auch die Kinetik des Sorptionsvorganges untersucht werden kann.

In den Jahren 1968 bis 1971 konnte ein solches Gerät mit Mitteln des *Schweizerischen Nationalfonds* (Kredit Nr. 4871.2) und der Stiftung der CIBA für naturwissenschaftliche, medizinische und technische Forschung entwickelt werden. Bau und Anwendung werden im folgenden kurz beschrieben.

Als günstige Lösung drängte sich die Kombination einer empfindlichen registrierenden Elektrowaage mit einem Konditionierungssystem durch ein zirkulierendes, indifferentes Gas auf. Abb. 1

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