69. Photochemistry of 4,4-Dialkoxy-2,5-cyclohexadienones

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Summary. Irradiation ($\lambda > 370$ nm) of 4,4-dimethoxy-2,5-cyclohexadienone (**1a**) in benzene affords mainly the ketene acetal **4a**, which then undergoes further rearrangement. The carbomethoxycyclopentenones **6** and **7** were isolated in modest yields (10–15%). It is conceivable that the latter results from decomposition of the unobserved bicyclohexenone **5a**, the formation of which could be expected by analogy to *e.g.* **1c** → **5c**. Compound **4a** is presumably formed *via* 1,2 hydrogen shift from the intermediate zwitterion **3a**. Under similar irradiation conditions 1,4-dioxa-spiro[4.5] deca-6,9-dien-8-one (**1b**) gave **4b** as the only definable product. In *i*-C_8H_{18} **1a** gave *p*-methoxyphenol (**8**) as the only product, most probably *via* hydrogen abstraction.

The photochemical behaviour of cross-conjugated cyclohexadienones represents a well investigated chapter in the field of organic photochemistry. Two reviews have appeared some time ago [1] [2] and new results on the subject continue to be published [3–5]. It has been shown *inter alia* that the different reactions observed depend on the reaction medium and on the substituents attached to the cyclohexadienone ring.

We now report our results on the photochemical behaviour of the 4,4-dialkoxycyclohexadienones **1a** and **1b**, an investigation stimulated by two facts: firstly there is only one short communication in the literature dealing with photoreactions of – in this case ring-alkylated – 4,4-dimethoxycyclohexadienones [6], and secondly compounds such as **1a** and **1b** are now becoming easily accessible by electrochemical synthesis [7–10]. In addition we compare the reactivity of **1a** and **1b** with the one of cyclohexadienone **1c** [11].

In contrast to other authors we have used light of $\lambda > 370$ nm in order to avoid light absorption by primary products, a problem often arising in photochemical studies of 2,5-cyclohexadienones. As a matter of fact the 0–0 transition in the absorption spectrum of **1a** and **1b** is shifted to longer wavelengths compared to **1c** (**1a** or **1b**: 413 nm, **1c**: 388 nm, solvent: *i*-C_8H_{18}). This agrees with the results of *Zimmerman* [12], that increasing the electronegativity of the substituents in the 4-position shifts the n-π^*-absorption maximum (and the 0–0 transition) of 2,5-cyclohexadienones to longer wavelengths.

Irradiation of **1a** in benzene or *t*-BuOH followed by chromatographic work-up gave a mixture of the carbomethoxy-2-cyclopentenones **6** and **7** in an overall yield of 10–15%. In water as a solvent **6** was formed exclusively and in slightly higher yields (20–25%). Monitoring the reaction in C_6D_6 by NMR. showed that the main product formed is the ketene acetal **4a** which has only limited stability in solution. For **1b**, the ketene acetal **4b** was the only clearly definable product when the reaction was monitored in C_6D_6 by NMR., while under the other conditions mentioned above only polymeric material was obtained after the work-up. When the reactions were monitored in C_6H_6 by IR. spectroscopy additional evidence for the concersions

1a → **4a** and **1b** → **4b** was afforded: the C=O stretching band at 1692 cm^{-1} decreased while a new band at 1720 cm^{-1} appeared. Finally a similar run with **1c** (C_6D_6, NMR.) showed the exclusive formation of 6,6-dimethylbicyclo[3.1.0]hex-3-en-2-one (**5c**), photostable under these conditions (*cf.* [11]). No such compound **5** was observed during or after irradiation of **1a** and **1b**. In hydrogen donating solvents, *e.g.*, *i*-C_8H_{18}, **1a** gave almost exclusively *p*-methoxyphenol (**8**) thus behaving similarly to related cyclohexadienones (*cf.* 4-trichloromethyl-4-methylcyclohexadienone [4]) with a good homolytic leaving group. In contrast **1b** again gave only polymeric material. These results are summarized – in detail for **1a** and briefly for **1b** and **1c** – in the scheme. The NMR. data of the products are given in the Table. They are in good agreement with those of other 4- and 5-substituted 2-cyclopentenones [13].

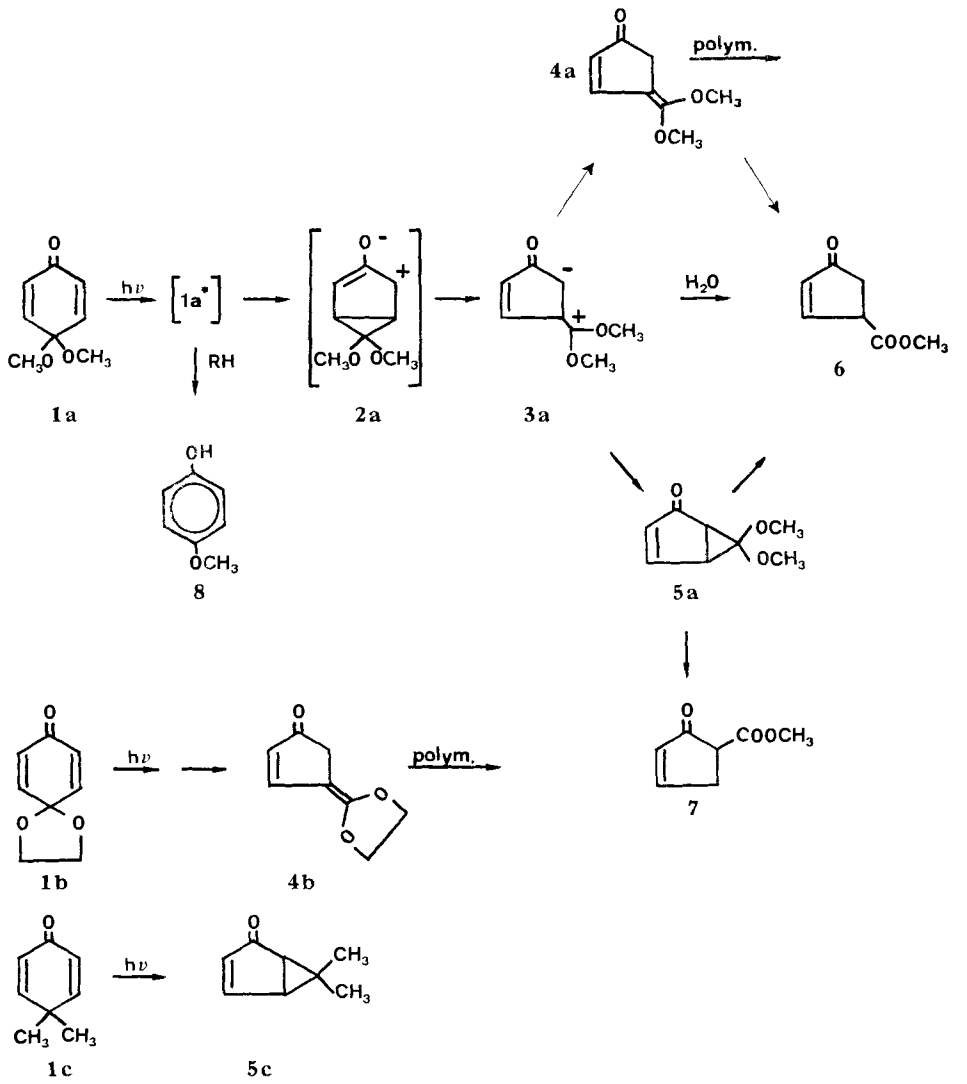
Table. *NMR. data of compounds* **4a**, **4b**, **5c**, **6** *and* **7** (*δ, multiplicity, relative intensity*)

Compound	Solvent	
4a	C_6D_6	7.95 (*d*) (1); 6.00 (*d*) (1) J = 5.4 Hz; 3.40 (*s*) (3); 3.33 (*s*) (3); 3.23 (*s*) (2)
4b	C_6D_6	8.00 (*d*) (1); 6.05 (*d*) (1) J = 5.5 Hz; 3.65 (*s*) (4); 3.15 (*s*) (2)
5c	C_6D_6	6.95 (*d*×*d*) (1); 5.80 (*d*×*d*) (1); 2.00 (*d*×*d*) (1); 1.75 (*d*×*d*) (1); 1.00 (*s*) (6) (*cf.* [11])
6	CCl_4	7.65 (*d*×*d*) (1) (J = 5.7 and 2.7 Hz); 6.15 (*d*×*d*) (1) (J = 5.7 and 2.4 Hz); 3.95 (*m*) (1); 3.75 (*s*) (3); 2.58 (*m*) (2)
7	CCl_4	7.85 (*d*×*t*) (1) (J = 5.6, 2.6 and 2.6 Hz); 6.08 (*d*×*t*) (1) (J = 5.6, 2.1 and 2.1 Hz); 3.85 (*m*) (1); 3.75 (*s*) (3); 3.00 (*m*) (2)

One should bear in mind that the normal reaction path in cyclohexadienone photochemistry, even for compounds containing one alkoxy substituent in the 4-position [14], consists in the conversion of, *e.g.* **2a** (mesoionic or nonionic, *cf.* [11]) to the bicyclic ketone **5a** *via* a sigmatropic rearrangement, the transition state of which can be represented by **3a**. Exceptions to this behaviour have been found in photoreactions of 4-hydroxy-4-alkylcyclohexadienones giving 4-acyl-2-cyclopentenones [15] and in the photoconversion of B-Nor-1-dehydrotestosterone acetate to an isomer containing a linear conjugated alkylidenecyclopentenone moiety [16]. Both these rearrangements are in formal analogy to the formation of **4a** from **1a**.

Although our results do not allow the exclusion of the reaction sequence **2a** → **5a** → **4a** (rearrangement of the unstable bicyclic ketone to the ketene acetal), we prefer the reaction sequence described in the scheme on the basis of the following arguments: a) due to the cumulative effect of two alkoxy groups, **3a** should become a stable intermediate; b) in water as solvent **6** is formed from **1a** exclusively, possibly due to partial trapping of **3a** (in other solvents **6** is usually formed in lower yields than **7**). In this context it must be remarked that trapping of **3a** with acrylonitrile was unsuccessful; c) although the analogous reaction **1a** → **6** was observed for the corresponding 2,6-di-*t*-butyl compound, no such reaction took place for the 2,5-di-*t*-butyl compound [6], wherein the hydrogen expected to undergo the 1,2 shift is replaced by a *t*-butyl group.

Scheme



Admittedly the independent synthesis of **5a** and study of its behaviour under the reaction conditions would represent the best way to obtain conclusive evidence on this point. Up to now all attempts in this direction failed.

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Experimental Part

Materials. **1a** [7], **1b** [8] [9] and **1c** [11] were synthetized according to the literature. The solvents used were of spectroscopic grade.

Photochemical experiments. The reactions were carried out under nitrogen using a HPK 125W mercury lamp (*Philips*) and a G.W.V. glass filter (transmission limit: 370 nm). In the runs monitored by NMR. the reactions were carried out in NMR. tubes (100 mg/0.5 ml). For preparative runs a standard irradiation set-up was used (1 g/100 ml). After about 8 h no starting material was left. For the isolation of **6** and **7** (mixture) the residue from **1a** of such a preparative run was chromatographed on a preparative thin-layer plate (silicagel, benzene/ethyl acetate 4:1). As both **6** and **7** slowly decompose in solution the ratios of isolated **6**/**7** from C_6H_6 or *t*-BuOH were not fully reproducible, varying between 1:2 and 1:1 (yield: 10–25%).

REFERENCES

[1] *K. Schaffner*, Advanc. Photochem. *4*, 81 (1966).
[2] *P. J. Kropp*, in 'Organic Photochemistry' part 1 (O. Chapman editor) chapter 1, Marcel Dekker Inc., New York 1967.
[3] *D. I. Schuster*, Pure and Appl. Chemistry, *41*, 601 (1975).
[4] *D. I. Schuster & K. V. Prabhu*, J. Amer. chem. Soc. *96*, 3511 (1974).
[5] *D. I. Schuster, G. C. Barile & K. Liu*, J. Amer. chem. Soc. *97*, 4441 (1975).
[6] *D. G. Hewitt & R. F. Taylor*, Chem. Commun. *1972*, 493.
[7] *A. Nilsson, A. Ronlan & V. Parker*, Tetrahedron Letters *1975*, 1107.
[8] *P. Margaretha & P. Tissot*, Helv. *58*, 933 (1975).
[9] *J. Heller, A. Dreiding, B. R. O'Connor, H. E. Simmons, G. L. Buchanan, R. A. Raphael & R. Taylor* Helv. *56*, 272 (1973).
[10] *G. L. Buchanan, R. A. Raphael & R. Taylor*, J. chem. Soc. Perkin I *1973*, 373.
[11] *J. S. Swenton, E. Sauerborn, R. Srinivasan & F. I. Sonntag*, J. Amer. chem. Soc. *90*, 2990 (1968).
[12] *H. E. Zimmerman, R. W. Binkley, J. J. McCullough & G. A. Zimmerman*, J. Amer. chem. Soc. *89*, 6589 (1967).
[13] *C. H. DePuy, C. E. Lyons & L. B. Rodewald*, J. Chem. & Eng. Data *11*, 102 (1966).
[14] *T. Matsuura*, Bull. Soc. chem. Japan *37*, 564 (1964).
[15] *E. R. Altwicker & C. D. Cook*, J. Org. chemistry *29*, 3087 (1964).
[16] *G. Bozzato, H. P. Throndsen, K. Schaffner & O. Jeger*, J. Amer. chem. Soc. *86*, 2073 (1964).

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70. 3-Alkyl-1-benzoxepin-5-on-Derivate und 2-Alkyl-1,4-naphthochinone aus 2-Acylaryl-propargyläthern

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3-Alkyl-1-benzoxepin-5-one derivatives and 2-alkyl-1,4-naphtoquinones from 2-acylaryl propargyl ethers. – *Summary.* It was found that 3-alkyl-1-benzoxepin-5(2*H*)-ones of type B can be synthesized by treating 2-acylaryl propargyl ethers of type A with sodium methylsulfinyl methide (NaMSM, dimesyl sodium) (*Scheme 13*). Oxepinone derivatives of type B undergo ring contraction with base (also NaMSM) to yield the quinol derivatives C which, oxidize (during work-up), if R^2 = H, to the 1,4-naphthoquinones D (*Scheme 13*).

The propargyl ethers used are listed in *Scheme 1*. The naphthalene derivatives **1** and **3** give oxepinones (*E*-**9** and a mixture of **14**/**15** respectively), whereas the expected oxepinone from **2** is transformed directly into the quinone **11** (*Scheme 2, 3* and *5*). Isomerizations of 2-acetylphenyl

[1] Auszug aus der Dissertation von *M. Mülly*, Universität Zürich 1975.