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PHOTOCHEMISTRY OF OXIRANE-SUBSTITUTED 2,4-CYCLOHEXADIENONE DIELS-ALDER DIMERS

Hans-Dieter Becker*, Bernd Ruge, and Tommy Westlöf
Department of Organic Chemistry, Chalmers University of Technology and
University of Gothenburg, S-402 20 Gothenburg, Sweden

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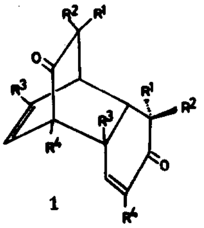
Diels-Alder dimerization of 2,4-cyclohexadienones gives compounds of structure 1 which, upon UV-irradiation (λ>300 nm), isomerize to cage compounds 2 in excellent yields.[1,2] This intramolecular cyclization is of analytical value because the C_2 symmetry of the photoproducts 2 confirms both the endo configuration and the structural orientation of the Diels-Alder dimers 1. When the photoreaction is monitored UV-spectroscopically, the expected decrease of absorption is observed in all cases.[3]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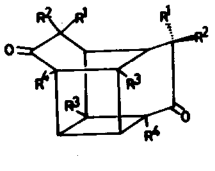
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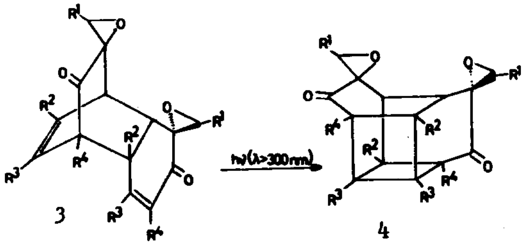
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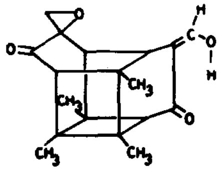
We have now studied the photochemical intramolecular cyclization of the spiro-oxirane-substituted Diels-Alder dimers 3a-d[4] in order to confirm their structures. Thus, irradiation of 3a (λ_{max} 312 nm; ε 350; 1 g in 65 ml ethanol; 18°; Pyrex immersion well apparatus; high-pressure mercury lamp, Philips HPK 125 W; N_2) for 2 hrs gave the cage compound 4a in 70 % yield. Irradiation in similar fashion of dimers 3b-d gave the corresponding cage compounds 4b-d (see Table 1). The structures of all new compounds are supported by elemental analyses and spectroscopic data (UV; IR; NMR; MS).

By comparison with the earlier reported formation of 2, the yields of 4 were fair or moderate. Monitoring the progress of the photochemical reaction of dimers 3 by UV-spectroscopy revealed, quite unexpectedly, a rapid increase of absorption around 310 nm. This indicated the formation of by-products which, conceivably due to their strong UV absorption, impaired the conversion of 3 into 4. Extraction with base of the reaction mixture from the irradiation of 3a led to the isolation of traces of 4,5-dimethylsalicylaldehyde (11) and, in 5 % yield, the novel asymmetric cage compound 5 (mp 220°). It was easily shown that 5 derived from 4a by photochemical isomerization of one oxirane group.[6] The structure of 5 is based on the following NMR-spectroscopic data. In $CDCl_3$ (δ, ppm): 1.05,s,6H; 1.06,s,3H; 1.18,s,3H; 1.55,s,1H; 2.72,s, 2H; 2.81,s,1H; 2.95,d,J_{AB} 6.5 cps,1H; 3.27,d,J_{AB} 6.5 cps,1H; 7.45,s,1H; 11.5, broad s,1H. The UV maximum of a 2.5 x 10^{-5} molar solution of 5 in ethanol at 310 nm has an ε-value of 18,000 i.e. the molar absorption of 5 is about 50 times stronger than that of 3a and more than 100 times stronger than that of its precursor 4a. The concentration dependence of the position of the UV-maximum (Fig 1A) indicates that 5 at a concentration of 2 x 10^{-5} mole/liter in ethanol is about 90 % ionized.

Table 1. Spiro-epoxy-substituted Cage Compounds 4

4	R^1	R^2	R^3	R^4	mp	% yield
a	H	CH_3	CH_3	H	294-300	70
b	H	CH_3	H	CH_3	229-233	58
c	H		H	CH_3	242-244	20
d	benzyl	H	H	H	204-206	35



5

The acidic properties of 5 finally facilitated its convenient preparation by the following experimental design. A chloroform solution of 3a (.6 g/300 ml) was irradiated in the presence of a layer of 4 N NaOH (50 ml) placed above the light-exposed region. Agitating the solutions gently by a slow stream of N_2, introduced through a sintered glass disk at the bottom of the photoreactor, continuously removed the strongly UV absorbing secondary photoproduct 5 and accumulated the 5-enolate in the alkaline layer. The free enol 5 was then readily obtained in 50 % yield by acidification with dilute H_2SO_4.

This experiment turned out to be essential for the preparation of 5 in reasonable yields. In the absence of base, prolonged irradiation of 3a resulted in the isomerization of the remaining oxirane group in 5. Thus, irradiation of 3a (300 mg) in ethanol (100 ml) for 24 hrs gave the new cage compound 6 (mp 233-235°; 40 % yield) which, because of its C_2 symmetry, exhibits an NMR spectrum of striking simplicity. [In $CDCl_3$ (δ, ppm): .99,s,12H; 2.18,s,2H; 2.69,s, 2H; 7.33,s,2H; ~12, broad s,2H.] Like 5, compound 6 exhibits a UV maximum whose position is concentration dependent (Fig. 1 B).

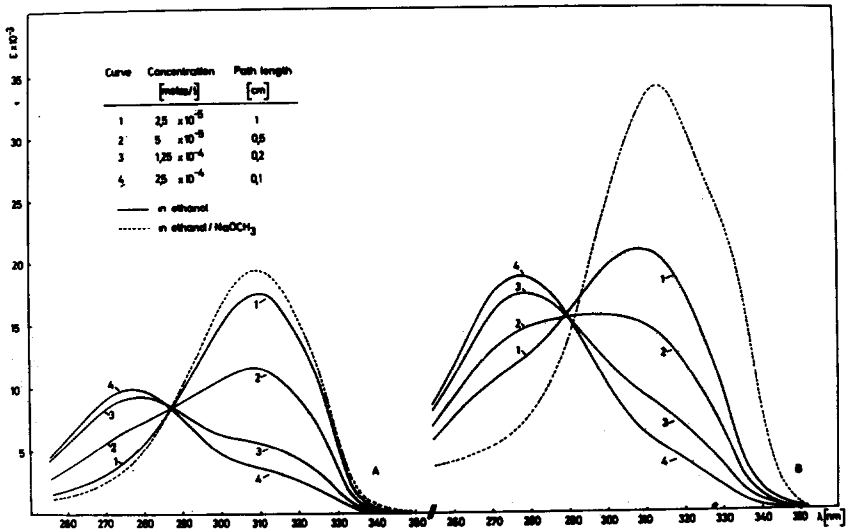
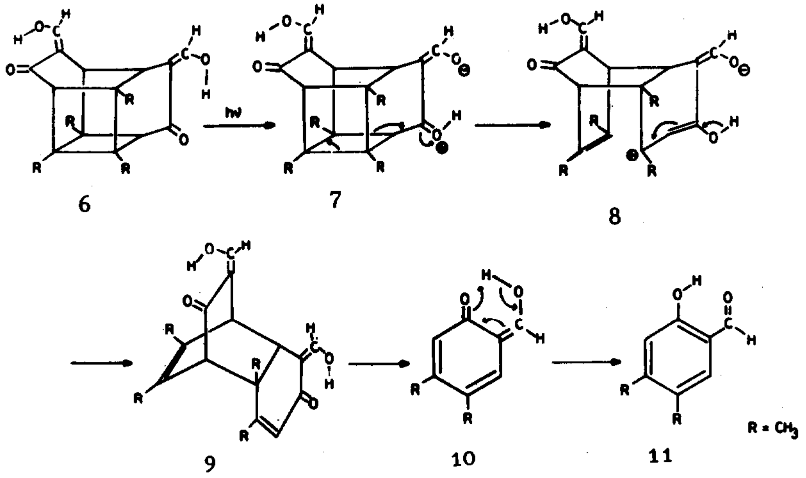


Fig. 1 UV-spectra showing enol-enolate equilibria of 5 (A) and 6 (B)

As for the traces of 4 5-dimethylsalicylaldehyde 11 obtained by irradiation of 3a, we found it to be formed by photochemical fragmentation of 6. Presumably, cage compound 6 upon irradiation undergoes intramolecular proton transfer (see Scheme 1) resulting in the cleavage of a cyclobutane ring to give a Diels-Alder dimer 9 which, for thermodynamic reasons, dissociates to give 11. The non-photochemical conversion of 6 into 11, accomplished by treatment with trifluoroacetic acid at 60°, lends support to this mechanism.

Scheme 1



In summary, we conclude that spiro-epoxy-substituted 2,4-cyclohexadienone Diels-Alder dimers 3 represent a novel heterochromophoric system which undergoes the photoisomerizations $3 \rightarrow 4 \rightarrow 5 \rightarrow 6 \rightarrow\rightarrow 11$ with a high degree of selectivity.

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References and Footnotes

1. H.-D. Becker and A. Konar, Tetrahedron Letters 5177 (1972).
2. T. Iwakuma, K. Hirao, and O. Yonemitsu, J. Amer. Chem. Soc., 96, 2570 (1974).
3. H.-D. Becker, Liebigs Ann. Chem., 1675 (1973).
4. For dimer 3b, see E. Adler, S. Brasen, and H. Miyake, Acta Chem. Scand. 25, 2055 (1971). Dimers 3a (mp 194°), 3c (mp 141°) and 3d[5] (mp 154°) were prepared analogously by periodate oxidation of 4,5-dimethylsalicylalkohol, 3-methyl-5-cyclohexylsalicylalkohol, and benzyl-(2-hydroxyphenyl)-carbinol,[5] respectively; (H.-D. Becker and T. Bremholt, unpublished results).
5. cf. H.-D. Becker and T. Bremholt, Tetrahedron Letters 197 (1973)
6. cf. J.R. Williams, G.M. Sarkisian, J. Quigley, A. Hasiok, and R. VanderVennen, J. Org. Chem., 39, 1028 (1974).