Tetrahedron Letters No. 44, pp 4215 - 4218, 1971. Pergamon Press. Printed in Great Britain.

PHOTOCHEMICAL DIMERIZATION OF 2,4-CYCLOOCTADIENONE

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(Received in USA 10 August 1971; received in UK for publication 1 October 1971)

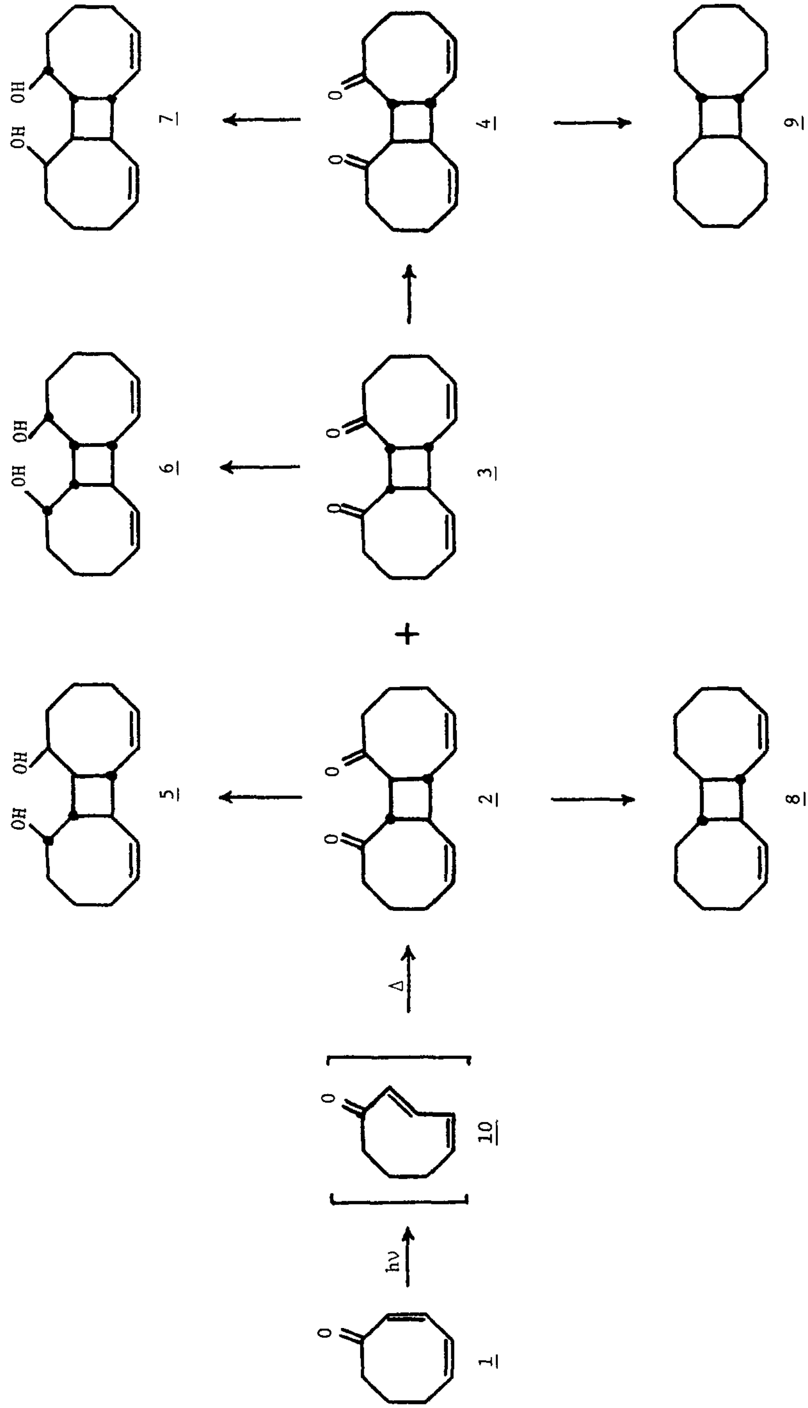
Cantrell recently reported[1] that u.v. irradiation 2,4-cyclooctadienone (1) in methanol or ether gave in low yield (6-10%) a dimer, m.p. 173-174°. The proposed head-to-head *cis-anti-cis* structure (as in 4) was based on spectral data, recovery of starting dimer after treatment with methanolic sodium methoxide and relatively slow cleavage by lead tetraacetate of the diester diol obtained by hydrogenation, Baeyer-Villiger oxidation, hydrolysis and esterification of the dimer.

We wish to report that irradiation of 1 in benzene using a 350 mμ source[2] resulted in the rapid disappearance of starting material and the formation in high yield (85%) of a mixture of two dimers, which were readily separated by fractional crystallization from ethyl acetate. Dimer 2 (33%) had the same physical properties as those described for Cantrell's dimer[1]: m.p. 174.5-175.0°; i.r. (KBr) 1698 (C=O), 685, 722 cm^{-1} (*cis* C=C); n.m.r. ($CDCl_3$) τ 4.3 (4H, multiplet), 6.6 (2H, multiplet), 7.3 (2H, multiplet), 7.4-8.6 (12H, multiplets).[3] The dimer prepared by irradiation of 1 in methanol was found to be identical[4] to dimer 2. Dimer 3 (52%), m.p. 89-90°, had the following spectral properties: i.r. (KBr) 1695 (C=O), 720 cm^{-1} (*cis* C=C); n.m.r. ($CDCl_3$) τ 4.2 (2H, multiplet), 4.6 (2H, multiplet), 5.8 (1H, triplet, J=9 Hz), 6.5 (1H, multiplet), 6.7-8.8 (14H, multiplets).

Treatment of either 2 or 3 with methanolic potassium hydroxide at room temperature for 50 hours resulted in epimerization to the same dimer, 4[5]: m.p. 126-127°; i.r. (KBr) 1692 (C=O), 718, 732 cm^{-1} (*cis* C=C); n.m.r. ($CDCl_3$) τ 4.3 (4H, multiplet), 6.0 (2H, doublet of doublets, J=7 and J=2 Hz), 6.6 (2H, multiplet), 7.1-8.6 (12H, multiplets). The epimerization could also be effected under the conditions described by Cantrell[1]. Epimerization to the same dimer (4) indicates that 2 and 3 differ only in their configuration at the cyclobutyl positions alpha to the carbonyl groups and that either one or both ring fusions are *trans*[6]. This result invalidates the *cis-anti-cis* structure proposed previously[1] for the dimer with m.p. 174°, but it should be noted that dimer 2 would be expected to give the same results in the Baeyer-Villiger experiment as described.[1]

Support for the proposed structures of the dimers was obtained by examining the i.r. spectra of the unsaturated diols 5, 6 and 7, the major products from sodium borohydride reduction of 2, 3 and 4 respectively. The spectrum of a dilute (0.005M) carbon tetrachloride solution of each of the diols was examined for the presence of intramolecular hydrogen bonding. The unsaturated diols were then hydrogenated and the spectra again examined to determine if the intramolecular hydrogen bonding was the result of an OH····OH or a transannular OH····π interaction. Diol 5, m.p. 116-117°, exhibited only free hydroxyl at 3630 cm^{-1}. This result is consistent with the *trans-anti-trans* fusions of the rings and the pseudo-axial configurations of the hydroxyl groups. Diol 6, m.p. 132-133°, exhibited both OH····OH (3450 cm^{-1})[9] and OH····π bonding (3530 cm^{-1}).[10] Hydrogenation gave tetrahydro 6 which exhibited OH····OH bonding (3475 cm^{-1}) and a free hydroxyl (3620 cm^{-1}). These findings support the structure proposed for 6 in which one ring is fused *trans* and the other *cis* and the hydroxyl groups are *cis*. Diol 7, m.p. 107-108°, exhibited only OH····π bonding (3562 cm^{-1}) while tetrahydro 7 showed only free hydroxyl (3632 cm^{-1}) as expected for the structure with *cis-anti-cis* ring fusions. The results of these hydrogen bonding studies were entirely consistent with the structures proposed for dimers 2, 3 and 4.

To confirm the stereochemistry of the ring fusions in 2, 3 and 4, the dimers were converted to hydrocarbons and compared with known samples. A modified Wolff-Kishner reduction[11] of 2 gave diene 8, which was identical to the *trans-anti-trans* dimer of *cis*, *trans*-1,3-cyclooctadiene[12]. All attempts to convert 3 or tetrahydro 3, m.p. 105-106°, to hydrocarbons were unsuccessful presumably because of the close proximity of the carbonyl groups. Hydrogenation of 4 gave tetrahydro 4,[13,14] m.p. 67-68.5°, which was converted to a saturated hydrocarbon *via* the ethanedithiol ketalization-Raney nickel desulfurization method. The product, 9, m.p. 57-58°, was identical to the hydrogenation product of the *cis-anti-cis* dimer of *cis*,*trans*-1,3-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cyclooctadiene.[12] These conversions conclusively establish the ring fusions in 2 and 4 and as a consequence of the epimerization experiment the structure of 3 can only be as depicted.

Comparison of the photochemical dimerization of 2,4-cyclooctadienone (1) in benzene with the thermal dimerization of *cis,trans*-1,3-cyclooctadiene reveals two similarities: (a) only head-to-head dimers are isolated and (b) the two most abundant dimers in each investigation have *cis-trans*[15] and *trans-anti-trans* ring fusions. In the photochemical dimerization of *cis*-2-cyclooctenone, Eaton[7] has shown that *trans*-2-cyclooctenone, produced photochemically from the *cis*-isomer, undergoes a thermal cycloaddition to give the dimers. Cantrell[1] has presented evidence for the existence of *trans,cis*-2,4-cyclooctadienone (10), which is formed upon irradiation of the *cis,cis*-isomer. He has proposed that the dimerization proceeds *via* addition of an excited triplet of 1 to ground-state 1 whereas we prefer a mechanism in which two molecules of 10 undergo a thermal dimerization.

The authors acknowledge financial support from the National Research Council of Canada.

References

1. T.S. Cantrell and J.S. Solomon, *J.Amer.Chem.Soc.*, 92, 4656 (1970).
2. The 1% benzene solutions were irradiated for five hours in pyrex tubes using the Rayonet Model RPR-100 Reactor with sixteen 350 mμ lamps.
3. This dimer and all new compounds described in this report gave elemental analyses and spectral data in agreement with the assigned structures.
4. The i.r. and n.m.r. spectra were identical, the melting point of a mixture was not depressed and the t.l.c. behaviour with two different solvent systems was the same.
5. An analytical separation of the three dimers could be effected using silica gel t.l.c. with three passes of chloroform to give the following R_f's: 2, 0.50; 3, 0.40; 4, 0.36.
6. *Trans*-fused bicyclo[6.2.0]alkanones epimerize to the *cis*-fused ketones under alkaline conditions.[7,8]
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12. C.L. Osborn,D.J.Trecker, A. Padwa, W. Koehn and J. Masaracchia, *Tetrahedron Letters*, 4653 (1970. We wish to express our appreciation to Dr. Osborn for experimental details prior to publication of their full paper [A. Padwa, W. Koehn, J. Masaracchia, C.L. Osborn and D.J. Trecker, *J.Amer.Chem.Soc.*, 93, 3633 (1971)].
13. Tetrahydro 2 has m.p. 70-71°. This compound has been reported[1] as a syrup but if the ethanol used in the hydrogenation is completely removed this diketone will crystallize.
14. We intend to compare the tetrahydro products of 2, 3 and 4 with the photochemical dimers of 2-cyclooctenone[7] as the structures of the latter dimers have not been fully elucidated.
15. The allylic cyclobutyl hydrogens in dimer 3 are *trans* while the corresponding hydrogens in the diene dimer are *cis*. Note erratum: *Tetrahedron Letters*, 5034 (1970).