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PHOTOLYTIC TRANSFORMATIONS OF cis, cis-CYCLODECA-3, 8-DIENE-1, 6-DIONE

Jerry W. Stankorb and Kenneth Conrow

Department of Chemistry, Kansas State University, Manhattan, Kansas 66502

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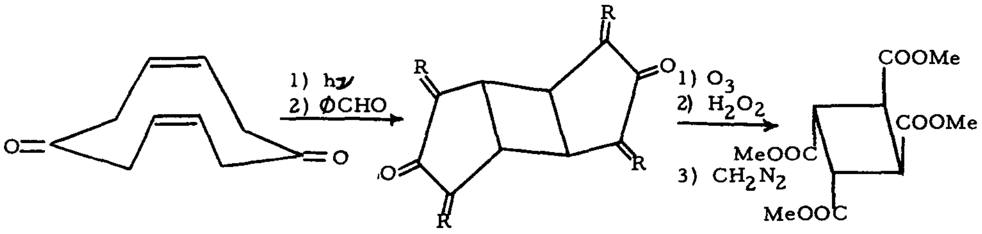
The recent communication by Shani (1) in which the photolysis of cis, cis-cyclodeca-3, 8-diene-1, 6-dione (I) is reported to give cis, syn, cis-tricyclo[5. 3. 0. $0^{2,6}$]decane-4, 9-dione prompts us to report results we had obtained independently which lead to the cis, - anti, cis (IIa) stereochemical assignment.

In our hands, using acetone as solvent and sensitizer, IIa (60%) along with three other products, was obtained after irradiating I for 2.5 hours (2). Under other conditions, as many as 10 different products have been shown to be present; of these only IIa, cis, trans-I, and 3, 4-divinylcyclopentanone have been identified. We are engaged in purification and identification of the other products.



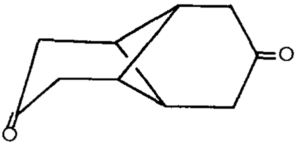
I

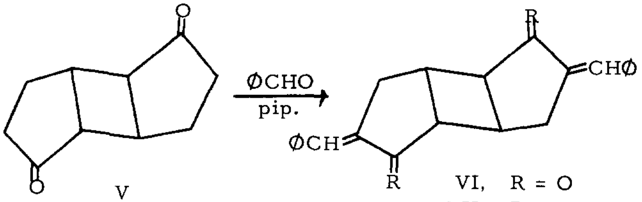
IIa R = H_2

IIb R = ϕCH

III

In order to prove the structure and stereochemistry of the tricyclic diketone IIa, a number of approaches were taken. The first successful approach proceeded by way of the tetrabenzylidene derivative (IIb), which was prepared from IIa using benzaldehyde and a catalytic amount of piperidine in refluxing ethanol (85%, mp 211-212°C) (3, 4). Upon ozonolysis of IIb, followed by oxidative workup and esterificiation with diazomethane, tetramethyl cyclobutane-1, 2, 3, 4-tetracarboxylate (III) was obtained (33%, mp 147°C; Lit. 144-145°C), whose ir and nmr spectrum was identical with that of the cis, trans, cis isomer reported (5, 6, 7), and distinct from that of the other isomers. Two facts exclude the possibility that this isomer is the product of epimerization during the ozonolysis and/ or esterification steps. 1) It is not the thermodynamically most stable isomer; equilibration produces the trans, trans, trans isomer. 2) Epimerization does not occur in an analogous preparation of the all cis isomer (8). The tricyclo[4. 4. 0. $0^{2,7}$] isomer IV could only give the trans, trans, trans-tetracarboxylate.

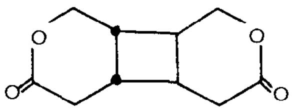

IV

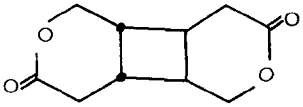


V

VI, R = O
VII, R = H_2

Proof by synthesis of the structure and stereochemistry of IIa was obtained by conversion of tricyclic diketone (V) (9) to its dibenzylidene derivative (VI) (87%, mp 269°C) (3), which upon reduction with $LiAlH_4/AlCl_3$ (1:2) (10) was converted to 3, 8-dibenzylidenetricyclo-[5. 3. 0. $0^{2,6}$]decane (VII) (3) (22%, mp 123-124°C). Oxidation of VII with $NaIO_4/KMnO_4$ in aqueous dioxane (11) afforded IIa (44. 4%), identical in all respects to the isomer isolated from the photolysate.

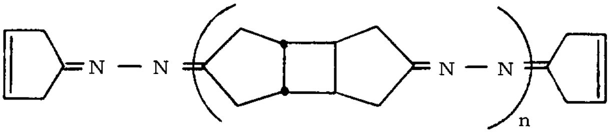

VIII


IX

In an earlier attempt at structure proof, the Baeyer-Villiger oxidation of the tricyclic diketone was performed. Reasoning that the symmetry of the tricyclo[4. 4. 0. $0^{2,7}$] system would require that only a single dilactone could arise, while the tricyclo[5. 3. 0. $0^{2,6}$] system should give two dilactones (VIII, IX), the dilactone was carefully investigated, but as yet only a single substance, (mp 211-212°C) (3) has been shown to be present.

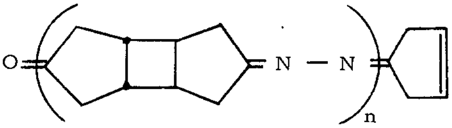
That our IIa is identical with Shani's product was shown by transketalization with 2, 2-dimethoxypropane and p-toluenesulfonic acid (12) to give a diketal which has the same mp, ir and nmr spectrum as that reported (1). The tricyclic diketone IIa was further characterized as an oxime [80%, mp 255-258°C(dec.)].

Since Shani's proof of structure and stereochemistry depends heavily on the isolation of an azine, which he formulates as a cyclic dimer, we have repeated that preparation. In our hands, reaction of the tricyclic diketone (IIa) and hydrazine hydrate (1:1 ratio) gave an amorphous compound in high yield [mp 295°C (preheated block), dec.)]; ν_{max}^{KBr} 3320 (w), 1740 (s), and 1655 (s) cm^{-1}. A mass spectrum of this azine, obtainable only at probe temperatures above the decomposition point, shows clusters of peaks not only at m/e 320 appropriate for the cyclic dimer as reported by Shani, but also at m/e 402, 480 and 562. Since the ir spectrum indicates residual carbonyl groups and terminal NH_2, we formulate the azine as linear polymer with carbonyl and hydrazone end groups. Upon electron impact and/or thermal decomposition on the probe, retrocyclization in the four-membered ring gives fragments (e.g. X and XI) of various sizes which account for the mass spectrum.



X

n = 0: m/e 160 (base peak); n = 1: m/e 320 (r.a. 12); n = 2: m/e 480 (r.a. 1.3)



XI

n = 1: m/e 242 (r.a. 25); n = 2: m/e 402 (r.a. 10); n = 3: m/e 562 (r.a. 0.8)

Evidently, I undergoes <u>cis trans</u> isomerization either prior to or concerted with photocyclization. IIa is obtained from I even under conditions where no photosensitization may be expected. Under these conditions, $n \rightarrow \pi^*$ excitation and intersystem crossing to a triplet state is followed by intramolecular energy transfer to one of the double bond π systems. Isomerization and cyclization may then ensue in this or subsequent excited states. In view of the variety of products which may serve as probes, this system is expected to be particularly informative in connection with intramolecular energy transfer during photochemical processes.

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