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PHOTO-INDUCED CYCLIZATION OF *CIS*,*CIS*-2,8-CYCLONONADIENONE *VIA* THE *CIS*,*TRANS* ISOMER

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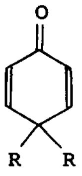
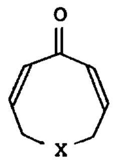
The photochemistry of cross-conjugated cyclic dienones is markedly influenced by ring size. The well-known rearrangement of 2,5-cyclohexadienones (I) is considered to involve the electronically excited dienones as the chemically reactive species.[1] In contrast, the photo-induced transformations of seven- and eight-membered dienones, IIa[2] and IIb,[3] were proposed and/or proved[3b] to proceed *via* certain ground-state molecules. The sterically constrained cis,-trans isomers IIIa and IIIb[3] or the zwitterion IVa[3b] were posturated as the precursors of the final products. Due to the thermal lability of the intermediates, however, none of the direct proof for the structure was given. We have examined the photolysis of the higher homologue, *cis*,*cis*-2,8-cyclononadienone (V), and obtained an unambiguous evidence for the formation of the reactive *cis*,*trans* isomer VI.

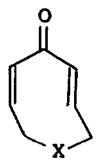


I



IIa, X = none

IIb, X = CH_2



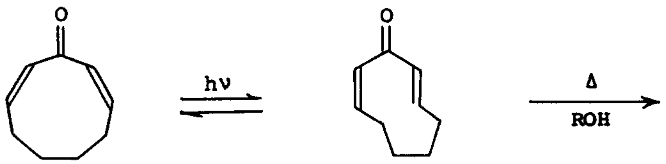
IIIa, X = none

IIIb, X = CH_2

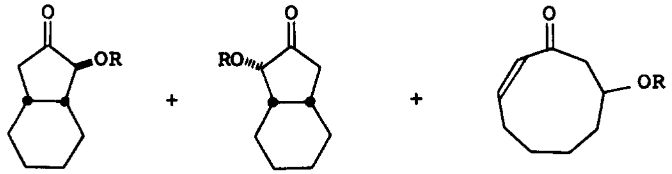
IVa, X = CH_2

IVb, X = CH_2CH_2

When a 1% solution of V[4] in acetic acid was irradiated[5] for 15 min, bicyclic polar adducts, *cis*- and *trans*-1-acetoxy-*cis*-hexahydro-2-indanones (VII and VIII), (60 and 19% yield, respectively) were obtained.[6] The structures



V VI



VII, R = Ac VIII, R = Ac XI, R = Me

IX, R = Me X, R = Me

were confirmed by converting the mixture into known cis-hexahydro-2-indanone[7] with zinc—acetic acid. Photolysis in a 1% methanolic solution afforded the similar bicyclic adducts IX (45%) and X (13%) along with the monocyclic product,[8] 8-methoxy-cis-2-cyclononenone (XI) (7%).

The intervention of a reactive ground-state species in the photo-induced reactions was demonstrated readily using ordinary techniques. Photolysis of V in a 1% cyclohexane solution for 5 min was followed by addition of a mixture of acetic acid and tetrahydrofuran (1:4) in the dark and allowance to stand for 5 min to produce a mixture of the acetoxy ketones, VII (14%) and VIII (6%) with recovery of the starting material V (76%). Similar treatment of the photolysate with methanol yielded a mixture of V (71%), IX (16%), X (5%), and XI (trace).

Thus the irradiation of V in an inert solvent was found to give a photo-equilibrated mixture of V and the reactive intermediate. The fairly high content (ca. 20%) of the new isomer and the modest stability in aprotic media permitted the spectral investigation of the structure. Since the nmr spectrum of the mixture in cyclohexane clearly showed four-proton multiplets in the vinylic region, the possible bicyclic structure IVb was excluded. The uv spectrum differed only slightly from that of V, indicating the dienone structure maintained. The ir spectrum (cyclohexane) exhibited new characteristic absorption at 1662 and 998 cm^{-1}. The occurrence of the carbonyl absorption at high wave-number (*cf*. 1642 cm^{-1} in V) results from the reduced conjugation with the carbon—carbon double bonds. The latter band should be ascribed to a strained *trans*-CH=CH group (*cf*. 1010 cm^{-1} in *trans*-2-cyclooctenone (neat)[9]).[10] Thus, combined with the foregoing chemical behavior, the initially formed species undergoing the polar addition with hydroxylic solvents was assigned as *cis*,*trans*-2,8-cyclononadienone (VI).

The stereospecific formation of the hexahydro-2-indanones having *cis* stereochemistry could be rationalized in terms of solvent-assisted conrotatory ring closure of the dienone VI. The detailed process could be analyzed as either a direct cyclization arising from the nucleophilic attack of the solvents ([$_{\omega}2_{s} + {}_{\pi}2_{a} + {}_{\pi}4_{s}$] and [$_{\omega}2_{s} + {}_{\pi}2_{s} + {}_{\pi}4_{s}$] modes),[11] or a stepwise transformation which involves the initial protonation at the carbonyl oxygen followed by the conrotatory cyclization and the nucleophilic attack of the solvents[3a] The closely related photochemical behaviors of IIa and IIb would strongly suggest that the reactions proceed by way of the *cis*,*trans* dienones IIIa and IIIb, respectively, as previously predicted.[3,12]

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(3) (a) R. Noyori and M. Kato, *ibid*., 5075 (1968); (b) J. K. Crandall and R. P. Haseltine, *J. Amer. Chem. Soc*., 90, 6251 (1968)

(4) Prepared from cyclononanone (*cf*. E. W. Garbisch, Jr., *J. Org. Chem*., 30, 2109 (1965)). λ_{max} (AcOH) 254 (log ε 4.01) and 335 nm (2.06); λ_{max} (MeOH) 247 (4.01) and 346 nm (2.03); λ_{max} (cyclohexane) 239 (4.06), 352 (1.84), 365 (1.91), 381 (1.85), and 399 nm (1.61).

(5) All photolyses were carried out externally using 200 W high-pressure

mercury arc through Pyrex filter under nitrogen atmosphere at room temperature.

(6) The assigned structure were supported by spectroscopic data (nmr, ir, and uv). All new compounds gave correct elemental analyses and/or molecular peaks and mass spectra.

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(8) *Cf*. (a) H. Nozaki, M. Kurita, and R. Noyori, Tetrahedron Lett., 2025 (1968); (b) R. Noyori, A. Watanabe, and M. Katô, *ibid*., 5443 (1968); (c) R. Noyori, H. Inoue, and M. Katô, Chem. Commun., 1695 (1970).

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(10) An ir spectrum (at -150°) of neat IIb which had been irradiated through NaCl windows showed a weak new absorption at 1020 cm^{-1} and a broadened carbonyl band.

(11) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N.Y., 1970.

(12) 2,11-Cyclododecadienone undergoes the photochemical deconjugation in both protic and aprotic media (*cf*. H. Nozaki, T. Mori, and R. Noyori, Tetrahedron, **22**, 1207 (1966)).

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