

SOLUTION PHOTOCHEMISTRY. XII.^{1,2}

NOVEL TRICYCLIC RING SYSTEMS FROM THE PHOTOLYSIS OF DIELS-ALDER ADDUCTS

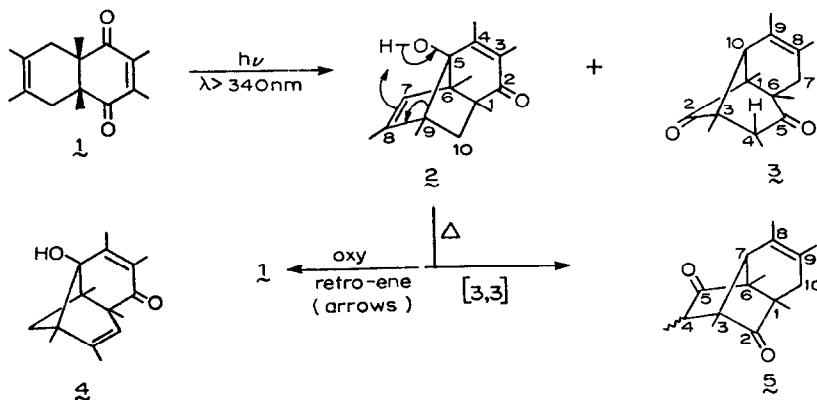
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The photolysis of Diels-Alder adducts of *p*-benzoquinone has proven to be a fruitful method for the synthesis of cage compounds (3) as well as sesquiterpene-like ring systems (4, 5, 6). In this paper we report additional novel ring systems accessible in this way.

Irradiation ($\lambda > 340$ nm) of dilute benzene solutions of the duroquinone-2,3-dimethylbutadiene Diels-Alder adduct 1 cleanly gave rise to products 2 and 3 (Scheme I) which could be isolated in 23% and 46% yield respectively by silica gel column chromatography (7).

Scheme I



Photoproduct 2, mp 101-102°, showed the following spectral characteristics: uv max (MeOH) 251 (ϵ 7400), 325 nm (ϵ 58); ir (CCl_4) 2.69 (OH), 5.98 (C=O) μ ; nmr (CCl_4) τ 4.62 (m, 1, vinyl), 7.79 (broad s, 1, OH, disappears with D_2O), 8.12-8.25 (m, 9, vinyl methyls), 8.43 (d, 1, $J = 12.5$ Hz, one of C_{10} methylenes), 8.92 (s, 3, methyl), 9.03 (d, 1, $J = 12.5$ Hz, one of C_{10} methylenes), 9.14 (s, 3, methyl), and 9.20 (s, 3, methyl). These data, while completely in accord with structure 2, did not rule out structure 4 whose formation is also mechanistically reasonable. This point was settled by means of a direct method single crystal X-ray structure determination which showed formula 2 to be correct.

Crystals of 2 are triclinic, $a = 7.832(2)$, $b = 13.797(3)$, $c = 6.731(1)$ Å, $\alpha = 98.21(3)$, $\beta = 101.36(2)$, $\gamma = 92.71(3)^\circ$, $Z = 2$, space group PT. The structure was determined with Cu K α scintillation counter data by direct methods and refined by full-matrix least squares, the final R being 0.061 for the 1774 observed reflections. Anisotropic thermal factors were used for C and O; H atoms were refined isotropically. A number of the bonds involved in the bridged structure are longer than normal with corresponding deviations from normal values for the bond angles. There is hydrogen bonding between the alcoholic oxygen and the carbonyl oxygen of the molecule in the neighboring unit cell. All other intermolecular contacts correspond to van der Waals interactions. A complete report of the crystallographic analysis will be published separately (8).

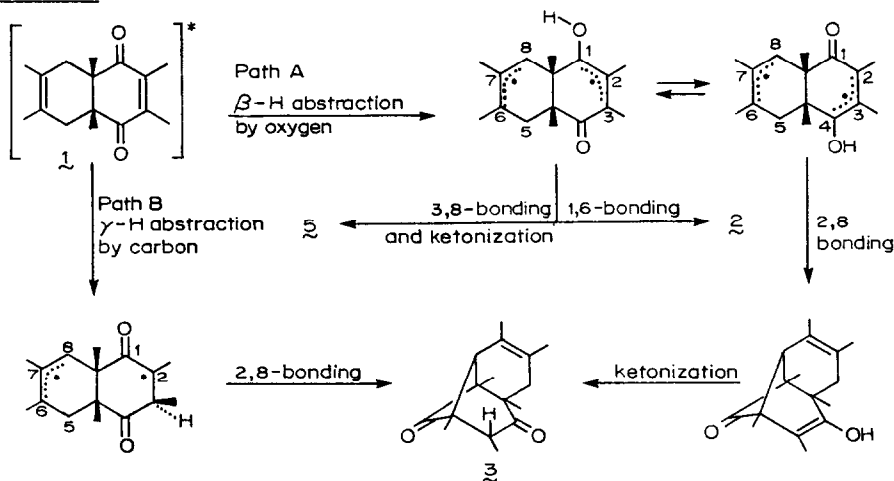
Thermolysis of photoproduct 2 at 280° led to a mixture of ene-dione 5 (50%) and original adduct 1 (20%) after column chromatography (Scheme I). A reaction analogous to the 2 \rightarrow 5 conversion has been observed previously in a similar system (5) and is formally the result of a [3,3] sigmatropic shift of the 5,9 bond followed by ketonization of the resulting enol (9). The formation of 1 from 2 represents a novel example of an oxy retro-ene reaction (10) (cf. arrows).

Photoisomer 3, a colorless liquid, exhibited the following spectra: uv max (MeOH) 246 (ϵ 660), 300 nm (ϵ 70); ir (CCl_4) 5.67 (four membered ring C=O) and 5.85 (six membered ring C=O) μ ; nmr (CCl_4) τ 7.57 (q, 1, $J = 7.5$ Hz, C_4 methine), 7.9-8.1 (m, 3, C_7 methylene and C_{10} methine), 8.25-8.40 (m, 6, vinyl methyls), 8.78 (s, 3, methyl), 8.95 (s, 3, methyl), 8.95 (d, 3, $J = 7.5$ Hz, C_4 methyl), and 9.03 (s, 3, methyl) (11).

Two possibilities may be envisaged for the photochemical formation of compound 3 from 1 (Scheme II). The difference between pathways A and B is that the formation of 3 via path A proceeds through its enol form while such is not the case with path B. In order to test which pathway is operative, Diels-Alder adduct 1 was irradiated both in tert-butyl alcohol- O-d and 1:1 dioxane- D_2O . In neither case did the 3 so produced contain deuterium (nmr, mass spectrum) (12). In addition, compound 5 began to appear as a photoproduct in dioxane- D_2O (ca. 5%) and as expected (5) it contained exactly one deuterium atom per molecule in the 4 position. These results provisionally rule out pathway A for the formation of 3 (but not

for $\underline{5}$ and $\underline{2}$) and indicate a competition between β -hydrogen abstraction by oxygen (4,5) and γ -hydrogen abstraction by carbon (13). It is tempting to speculate that these processes originate from $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ excited states respectively (14) although conformational effects due to the bridgehead methyl groups may also play a role. Experiments designed to clarify these points are in progress.

Scheme II



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9. Ene-dione 5, a colorless liquid, showed $n \rightarrow \pi^*$ uv max (MeOH) 292 nm (ϵ 70); ir (CCl_4) 5.72 (C=O) μ ; nmr (CCl_4) τ 7.93 (broad s, 1, C_7 methine), 7.99 (q, 1, $J = 7$ Hz, C_4 methine, disappears under deuterium exchange conditions), 8.09 (m, 2, C_{10} methylene), 8.28 (m, 3, vinyl methyl), 8.39 (broad s, 3, vinyl methyl), 8.87 (s, 3, methyl), 9.05 (s, 3, methyl), 9.17 (d, 3, $J = 7$ Hz, C_4 methyl, converted to broad singlet upon deuteration at C_4), and 9.28 (s, 3, methyl).
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11. The structure of compound 3 also follows from its thermal and base-catalyzed rearrangements. These reactions will be the subject of a future report once labeling studies designed to elucidate their mechanisms are completed.
12. Lack of incorporation due to steric hindrance of exchange is unlikely in view of the fact that the enolate of 3 is readily formed. J.R. Scheffer and R.E. Gayler, unpublished results.
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