

Novel Photochemical Reaction of *p*-Benzoquinone Derivatives. Transannular Addition and Quinone Ring Cleavage in 2,5-(Oct-4-eno)-*p*-benzoquinones {Tricyclo[8.2.2]-tetradeca-1(13),5,10-triene-12,14-diones}

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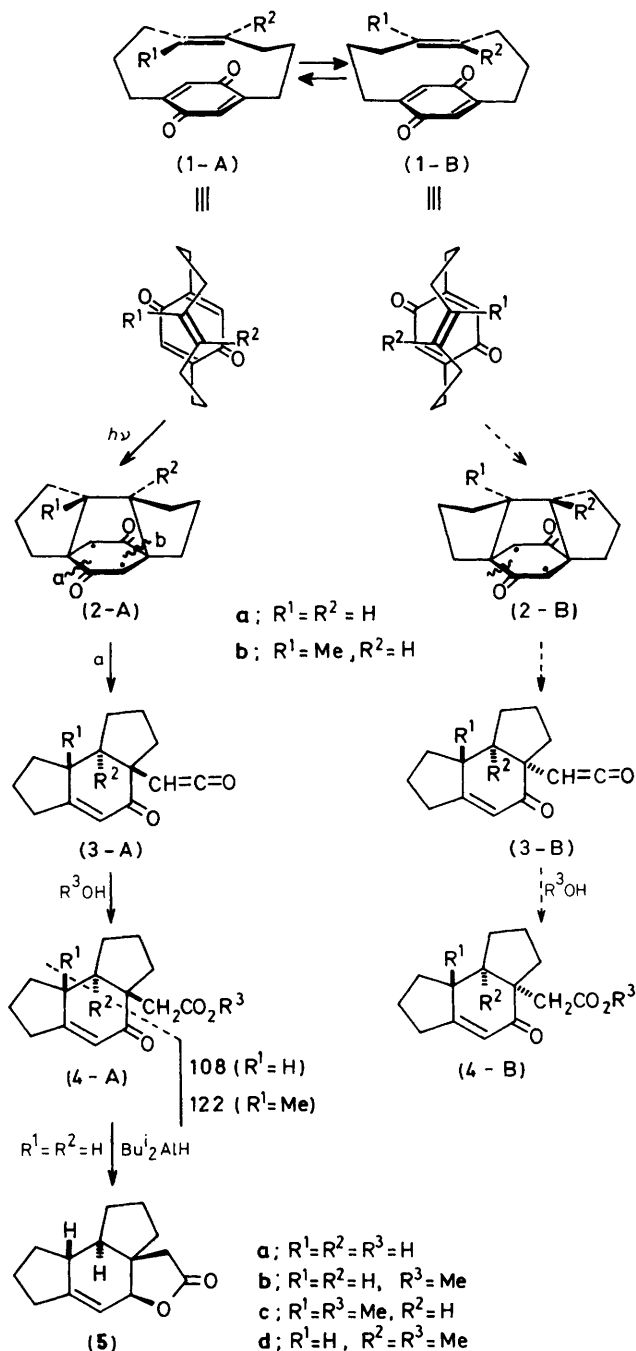
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2,5-(Oct-4-eno)-*p*-benzoquinone (**1a**) and its derivative (**1b**) undergo novel photochemical transformation giving quinone ring-cleaved, tricyclic carboxylic acid derivatives (**4-A**).

It is well established that the formation of oxetane and of cyclobutane are standard photoreactions of *p*-benzoquinone and its derivatives with olefins.¹ We recently found, however, a novel type of photoreaction for the bridged *p*-benzoquinones (**1**)² giving unexpected, quinone ring-cleaved products (**4-A**) stereoselectively, a reaction initiated by the cycloaddi-

tion of the double bond in the bridge to C-2 and C-5 of the quinone ring. Despite the fact that this reaction might result from the bridged structure of (**1**), it has revealed a new photoreactivity of the *p*-benzoquinone ring system.

When an aqueous acetonitrile solution of (**1a**) was exposed to sunlight or u.v. irradiation (> 330 nm), the orange colour



Scheme 1

due to **(1a)** quickly faded, and work-up afforded a carboxylic acid in 88% yield. Photolysis of **(1a)** in methanol led to the corresponding methyl ester in 91% yield. Spectral analysis and the formation of a γ -lactone upon Bu^i_2AlH reduction of the carboxylic acid permitted us to assign structures **(4a-A)** and **(4b-A)**, respectively to these products.[†]

The photochemical reaction of the monomethyl derivative **(1b)** in methanol similarly proceeded with ease and gave a

[†] Satisfactory spectral and analytical data were obtained for all new compounds.

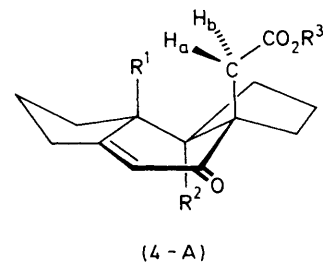


Figure 1

mixture of two isomeric esters in 32 and 50% yields. The major product was assigned structure **(4c-A)** and the minor product structure **(4d-A)**. The angular methyl proton signal of **(4c-A)** appeared at δ 1.11, 0.39 p.p.m. downfield from that of **(4d-A)**. This is consistent with the substituent effect on the chemical shift for the C-19 protons in steroids.^{3‡} In addition, the 500 MHz n.m.r. spectrum of **(4d-A)** exhibited signals presumably due to the three allylic protons at δ 2.4–2.8 which were well resolved from the other aliphatic proton signals whereas that of **(4c-A)**, as expected, showed signals due to only two protons in the same region.[§]

The present photochemical reaction may be rationalized as occurring by the addition of the double bond on the side chain to the C-2 and C-5 of the quinone ring giving the 1,4-biradical intermediate **(2-A)**, which is subsequently cleaved to generate the ketene derivative **(3-A)**. The addition of water or methanol to **(3-A)** affords the corresponding carboxylic acid or methyl ester. The formation of an isomeric mixture of **(4c-A)** and **(4d-A)** from **(1b)** can be readily accounted for in terms of the competing cleavage of bond (a) or (b) in the biradical intermediate **(2b-A)**; *i.e.*, cleavage at bond (a) leads to **(4c-A)** while the scission of bond (b) results in **(4d-A)**.

The proposed mechanism suggests that the ketene intermediate may be observed if the reaction is carried out in an aprotic medium, and this was indeed the case. The quinone **(1a)** or **(1b)** was pressed into a dry KBr disc for i.r. measurement and exposed to sun-light with the exclusion of moisture. The yellow colour of the disc due to the quinone was quickly bleached and the i.r. spectrum taken thereafter showed a strong absorption at 2110 cm^{-1} , substantiating the generation of the ketene.⁵

Examination of molecular models and also the known properties of [8]paracycloph-4-enes⁶ indicate that **(1)** will exist as an equilibrating mixture of two conformers **(1-A)** and **(1-B)**. The phototransannular reaction of the former will give the product **(4-A)** whereas the reaction of the latter will produce the isomer **(4-B)** as shown in Scheme 1. The photoreaction of **(1)**, however, cleanly afforded **(4-A)** without contamination by the isomer **(4-B)**. The stereochemical assignment was made primarily on the basis of nuclear Overhauser enhancement

[‡] As shown in Figure 1, the substituents R^1 and R^2 in **(4-A)** are in axial positions. The substituent effect for the C-19 protons in steroids suggests that the angular methyl proton signal of **(4c-A)** will appear 0.4–0.5 p.p.m. downfield from that of **(4d-A)**.³

[§] In the mass spectra of **(4-A)**, the fragment ion which might arise from the well documented retro-Diels–Alder cleavage of the cyclohexenone ring⁴ was invariably observed as the most abundant ion; *i.e.*, m/z 108 in the spectra of **(4a-A)**, **(4b-A)**, and **(4d-A)**, and m/z 122 in the spectrum of **(4c-A)**. These observations are also in accord with the assignment.

(n.O.e.) experiments (Figure 1).¶ As previously reported,⁷ the equilibrium between the conformers (1-A) and (1-B) would be displaced in favour of the former. Therefore, the selective formation of (4-A) might arise from the predominance of the conformer (1-A) in the starting quinone. However, it is also possible that the conformer (1-B) might be photochemically less reactive than (1-A). The study of the photochemical behaviour of related substrates in connection with the rotational isomerism is now under way and will be reported in due course.

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¶ Irradiation of the angular methyl protons of (4c-A) induced 13 and 6% n.O.e. in the diastereotopic protons H_a and H_b, whereas irradiation of those of (4d-A) induced virtually no n.O.e. in R¹ = H, H_a, or H_b. These observations indicate that R¹ and R² are *trans*, as also are R² and the CH₂CO₂Me group. The stereochemical assignment for (4a-A) was supported by n.m.r. studies on (5) using a shift reagent.

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