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# PHOTOCHEMICAL REARRANGEMENT OF CYCLOBUTENE DERIVATIVES FORMED BY PHOTOADDITION OF ACETYLENES TO NAPHTHOQUINONES

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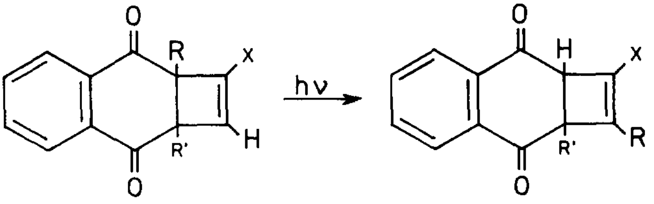
Recently we reported about the preparation of cyclobutene derivatives formed by photoaddition of various acetylenes to 1,4-naphthoquinones 1). We found that some of these compounds may undergo rearrangement under irradiation.

The photoisomerization of a cyclobutene derivative was first investigated by BÜCHI and BURGESS 2). They found that irradiation of eucarvone yields a photostationary mixture of two bicyclo[3.2.0]heptenone isomers. Other bicyclo[3.2.0]heptenones with various substituents show the same type of reaction 3,4). Another example is the photoisomerization of a bicyclo[4.2.0]octanone derivative 5). These photoisomerizations may be due to the steric conformation of non-planar β,γ-unsaturated ketones*).



I–VI Ia–VIa

| | R | R' | X |
|---|---|---|---|
| I | Ph | H | Ph |
| II | Me | H | Me |
| III | Me | H | H |
| IV | Me | Me | Me |
| V | Me | Me | H |
| VI | Me | Me | Ph |

Since the structure of the substituted 2a,3,8,8a-tetrahydrocyclobuta[b]naphthalene-3,8-diones (I-VI) are similar to non-planar β,γ-unsaturated ketones 7) they should exhibit this type of photorearrangement.

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*) This type of photoisomerization was observed recently with a cyclobutene derivative formed by photoaddition of dimethyl acetylene dicarboxylate to several benzo[b]thiophenes 6).

Irradiation of solution of compounds I - VI (100 mg in 100 ml benzene) for a period of one to ten hours using a 125 W high-pressure mercury lamp with Solidex filter $\lambda \geqq 302$ nm yields the isomeric cyclobutene derivatives Ia - VIa, respectively. Structures were confirmed unambiguously by comparison of the spectroscopic data with those of known 1) cyclobutene derivatives formed by photoaddition of acetylenes to naphthoquinones. For example compound IVa is identical to the cyclobutene derivative formed by the photoaddition of 2-methyl-1,4-naphthoquinone to 2-butyne as shown by identical IR, UV, NMR, mass spectrometric and analytical data 7,8).

The best method of following the photorearrangement was NMR-spectroscopy. The change of the chemical shift and coupling constants of the proton migrating from a cyclobutene ( ~3.6 τ ) to a cyclobutane ( ~6 τ ) position could be observed easily.

When the corresponding rearrangement products (Ia - Va) were irradiated for 10 hrs no starting materials (I - V) could be detected. This indicates that no equilibria exist between reactants and products such as were found with the bicyclo[3.2.0]heptenone derivatives 2,3,4) or that if equilibria exist they must strongly favor the formation of the rearrangement products (Ia - VIa).

Irradiation of V and VI yields two products each: Va, Vb and VIa, VIb, respectively. The ratio Va : Vb depends upon the reaction time, decreasing with prolonged irradiation, while the ratio VIa : VIb remains constant (VIb : VIa = 5.3).

Va (≡II) Vb*) (≡IIa) VIa VIb

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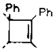
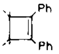
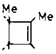
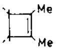
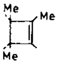
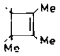
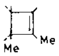
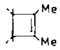
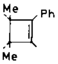
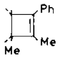
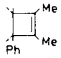
*) The formation of Vb may occur by direct rearrangement of V perhaps following a concerted mechanism. After 6 hrs irradiation of II, less than 1 % of IIa, but about 10 % of Vb from irradiation of V was found.

In general we observe the exchange of a methyl group from an $sp^3$-hybridized carbon atom with a proton from an $sp^2$-hybridized carbon atom. The only exceptions being the rearrangements of I to Ia and VIa to VIb which involve phenyl-proton and methyl-phenyl exchange, respectively.

Kinetic experiments with monochromatic light ($\lambda$ = 366 nm, $\bar{\nu}$ = 27300/cm) should yield more information about the mechanism. Under these conditions*) only $n\pi^*$ excitation occurs 7).

Table 1: Photorearrangement of the compounds I-VI with $\lambda$ = 366 nm a)

| | Starting material (A) | | Photoproducts (B) | | | |
|---|---|---|---|---|---|---|
| No. | Formula b) | $\epsilon$ (366 nm) | No. | Formula b) | $\epsilon$ (366 nm) | $\frac{B}{A+B}$ 100 c) |
| I |  | 380 | Ia |  | 1500 | < 1 |
| II |  | 140 | IIa |  | 170 | < 1 |
| III |  | 130 | IIIa |  | 140 | 9 |
| IV |  | 200 | IVa |  | 210 | 65 |
| V |  | 150 | Va,Vb |   | 140,170 | 78 |
| VI |  | 670 | VIa,VIb |   | - d) | 60 e) |

a) ~ 0.25 mMol starting material were irradiated in 10 ml benzene for 6 hrs (under these conditions all incident light will be absorbed)

b) the quinone parts of the molecules are not shown

c) determined by NMR spectroscopy

d) not determined

e) only 3 hrs reaction time

The photoconversions of I-VI to Ia-VIa do not depend upon the extinction coefficients as postulated for the bicyclo[3.2.0]heptenone systems 2). The lack of equilibria in our reactions requires a different explanation.

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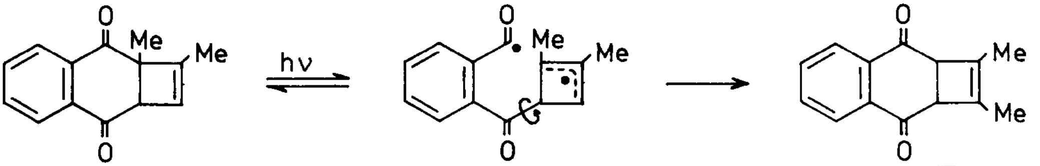
*) The photorearrangement can also be induced by irradiation with $\lambda \geq 405$ nm ($\bar{\nu}$ = 24700/cm) as shown with compound VI. Therefore in the reaction of p-quinones with acetylenes small amounts of rearrangement products can be found 9).

The primary and most important step seems to be the Norrish type I cleavage yielding an allylic diradical as proposed by BÜCHI and BURGESS [2]. It is well known that α-cleavage occurs preferentially between the carbonyl group and the more heavily substituted α-carbon [10]. In the case of the compounds I-VI the cleavage will occur only when the proton at the α-carbon is substituted by a methyl or phenyl group. This explains the inconvertability of the rearrangement products to the starting material due to the absence of α-cleavage. On the other hand α-cleavage is possible in compound VIa and VIb explaining the equilibrium between them.



II IIa

The recombination of the allylic diradical will be determined by the most reactive radical center following the sequence $=\dot{C}-H > =\dot{C}-Me$. This demands that the lifetime of the biradical is long enough to allow the rotation of the cyclobutene system. The ratio of the photoproducts to starting materials as given in Table 1 seems to depend upon substituents at the cyclobutene system - but further investigation is necessary to explain their influence.

## References

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