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PHOTO-REACTIONS OF 2-HYDROXYCYCLOOCTATRIENONES (π-HOMOTROPOLONES)

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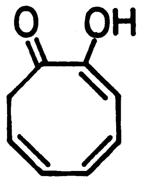
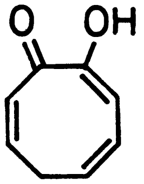
Irradiation of 2-hydroxy-2,4,6-cyclooctatrienone (1,7-π-homotropolone) (1) afforded 1-hydroxybicyclo[3.3.0]octa-3,6-diene-2-one (9), whereas 2-hydroxy-2,4,7-cyclooctatrienone (5,7-π-homotropolone) (2) did 1-hydroxybicyclo[3.3.0]octa-3,7-diene-2-one (12) and 3-hydroxybicyclo[3.3.0]octa-3,7-diene-2-one (13). 3-Bromo derivatives gave similar results. The mechanisms of these reactions as well as tropolone-photocyclization are discussed.

We have recently reported the synthesis of 2-hydroxy-2,4,6-cyclooctatrienone (1) and 2-hydroxy-2,4,7-cyclooctatrienone (2) which, we infered, have some homoconjugation by non-bonded interaction and hence deserve to be called π-homotropolones.[1,2]

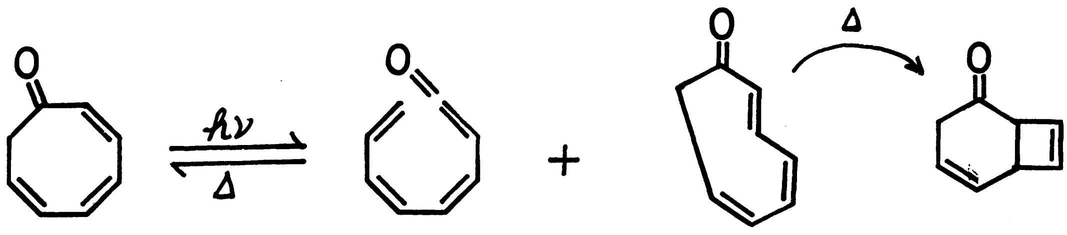


(1)

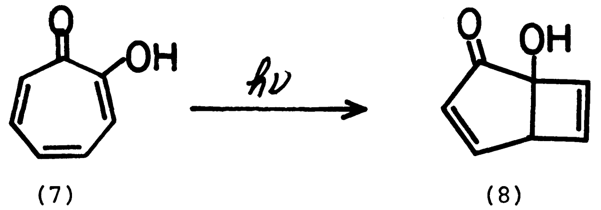


(2)

2,4,6-Cyclooctatrienone (3) is known to produce on photo-irradiation the triene ketene (4) and (E,Z,Z)-2,4,6-cyclooctatrienone (5), the latter being the precursor of the bicyclic ketone (6),[3] whereas tropolone (7) affords the bicyclic ketone (8).[4] Because (1) and (2), particularly (1), are structurally related to (3) and (7), it may be of interest to examine the photochemical behavior of these compounds.



(3) (4) (5) (6)

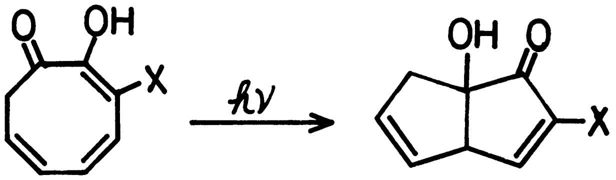


(7) (8)

Irradiation[5] of (1)[1] in ether for one hour resulted in the complete disappearance of the material and after chromatography on silica gel afforded 1-hydroxybicyclo[3.3.0]octa-3,6-diene-2-one (9) as the single product in 60% yield [IR (liquid); ν=3380, 1702 cm^{-1}; UV (methanol): λ=220 (ε 6210), 331 nm (41); ^{1}H-NMR-NMDR ($CDCl_3$, 100 MHz): δ=2.63 (2H, m), 3.77 (1H, dddd, J=2.5, 2.3, 1.7, 1.0 Hz), 3.86 (1H, br. s, OH), 5.65 (1H, dddd, 5.8, 1.9, 1.0, 1.0), 5.75 (1H, ddd, 5.8, 2.3, 1.9), 6.03 (1H, dd, 6.0, 1.7), 7.55 (1H, dd, 6.0, 2.5)]. The spectral data are compatible with the assigned structure. 3-Bromo-2-hydroxy-2,4,6-cyclooctatrienone (10)[1] gave the similar product (11) in 69% yield [^{1}H-NMR ($CDCl_3$, 60 MHz): δ=2.69 (2H, m), 3.62 (1H, br. s, OH), 3.74 (1H, br. d, J=2.8 Hz), 5.75 (2H, br.), 7.69 (1H, d, 2.8)].

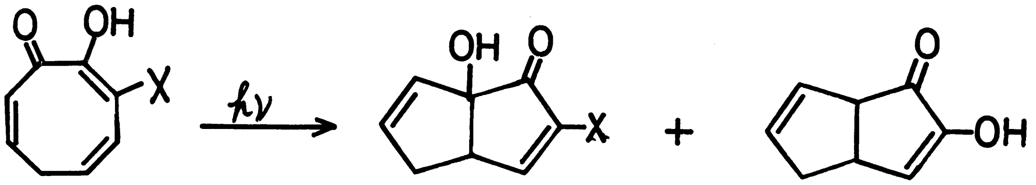
Somewhat different from (1), irradiation of (2)[2] in ether afforded two products, 1-hydroxybicyclo[3.3.0]octa-3,7-diene-2-one (12) and 3-hydroxybicyclo[3.3.0]octa-3,7-diene-2-one (13), in 44% and 27% yield, respectively [(12); IR (liquid): ν=3390, 1703 cm^{-1}; UV (methanol): λ=222 (ε 6610), 338 nm (120); ^{1}H-NMR-NMDR ($CDCl_3$, 100 MHz): δ=2.20 (1H, dddd, J=17.5, 3.0, 2.4, 2.0 Hz), 2.97 (1H, dddd, 17.5, 9.6, 2.4, 2.0), 3.28 (1H, br. s, OH), 3.32 (1H, dddd, 9.6, 2.4, 2.0, 1.8), 5.62 (1H, ddd, 5.5, 2.4, 2.4), 5.87 (1H, ddd, 5.5, 3.0, 2.0), 6.11 (1H, dd, 6.0, 1.8), 7.48 (1H, dd, 6.0, 2.4); (13): IR (liquid): ν=3340, 1702, 1645 cm^{-1}; UV (methanol): λ=259 (ε 6030), 313 nm (190); ^{1}H-NMR ($CDCl_3$, 90 MHz): δ=2.19 (1H, br. d, J=17 Hz), 2.71 (1H, br. dd, 17, 10), 3.4 (2H, m), 5.6 (2H, m), 5.98 (1H, br. s, OH), 6.39 (1H, d, 2.6)]. 3-Bromo-2-hydroxy-2,4,7-cyclooctatrienone (14)[2] gave (15) in 15% yield [^{1}H-NMR ($CDCl_3$, 60 MHz): δ=2.15 (1H, br. d, J=15.5 Hz), 2.71 (1H, ddt, 15.5, 9.0, 2.2), 3.44 (2H, m, decreased to 1H by adding D_2O), 5.50 (1H, m), 5.91 (1H, m), 7.56 (1H, d, 2.4)].

Change of the solvent from ether to acetone had little influence on the products and the yeilds in these reactions.



(1) X=H
(10) X=Br

(9) X=H
(11) X=Br



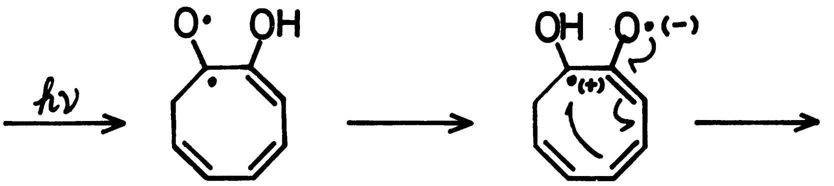
(2) X=H
(14) X=Br

(12) X=H
(15) X=Br

(13)

These results are distinctly different from the behavior of 2,4,6-cyclooctatrienone (3)[3], but they rather resemble that of tropolone (7).[4] In sharp contrast with the single product from (1), irradiation of the ethyl ether (16)[6] at the same condition employed for (1) and (2) gave a very complex mixture of products.[7] Therefore, it is apparent that the presence of a hydroxy group in (1) and (2) plays a decisive role on the reaction course. The formation of (9) from (1) may proceed via the diradicals (17) and (18) (or the corresponding ionic species such as (18')). Similarly, the common intermediate for (12) and (13) from (2) may be the diradical (19) in which two cyclization paths leading to bicyclo[3.3.0]octane system are possible.

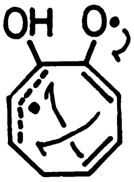
(1)



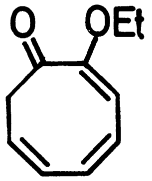
(9)

(17)

(18)
(18') (ionic)



(19)

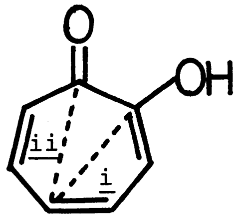


(16)

The results here obtained raise a question on the mechanism of the photocyclization of tropolone (7) to the bicyclic ketone (8). There can be two modes for the cyclization; (i) cyclization occurs at C-2 and C-5 (dotted line i) in a manner of valence tautomerization, whatever is the real cyclization-mechanism (diradical, ionic, or concerted); (ii) cyclization occurs at C-1 and C-5 (dotted line ii) in a similar manner considered for (1) and (2).

The mode (i) is the case when the hydroxy group is masked as exemplified by the photo-cyclization of 2-methoxytropone (20) to the bicyclic ketone (21).[8] Ebine, et al., reported that irradiation of 2,3-benzotropolone (22) gave rise to the tricyclic ketone (23).[9] Although the authors have briefly suggested a mode (i) cyclization followed by a rearrangement for the reaction mechanism, it seems, in the light of our results, that the mode (ii) is working in the reaction.

Our results suggest that the photo-cyclization of tropolone (7) itself likely proceeds on mode (ii), though the symmetric nature of (7) due to highly mobile tautomerism does not permit a distinction to be made experimentally between the two modes.



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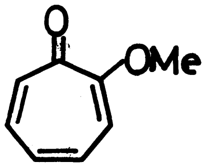

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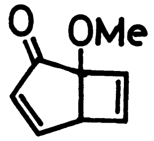

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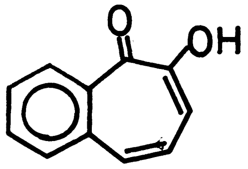

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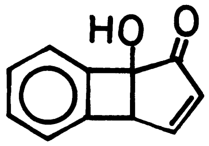

(23)

References and Notes

1) Y. Kitahara, M. Oda, and S. Miyakoshi, Tetrahedron Lett., 4141 (1975).

2) Y. Kitahara, M. Oda, S. Miyakoshi, and S. Nakanishi, Tetrahedron Lett., 4145 (1975).

3) L. L. Barber, O. L. Chapman, and J. D. Lassila, J. Amer. Chem. Soc., 91, 531 (1969), and references therein.

4) a) W. G. Dauben, K. Koch, and W. E. Thiessen, J. Amer. Chem. Soc., 81, 6087 (1959); b) E. J. Forbes and R. A. Dipley, Chem. & Ind., 589 (1960); c) A. C. Day and M. A. Ledlie, Chem. Commun., 1265 (1970).

5) The irradiations were performed using a 100 W high pressure mercury lamp as the light source through a water cooled pyrex probe.

6) The compound (16) was prepared by the reaction of (1) with $Et_3O^+BF_4^-$ in the presence of t-BuOK in THF (50% yield).

7) The reaction mixture showed at least seven spots on a silica gel TLC.

8) W. G. Dauben, K. Koch, O. L. Chapman, and S. L. smith, J. Amer. Chem. Soc., 83, 1768 (1961); 85, 2616 (1963).

9) M. Yoshioka, I. Saito, M. Hoshino, and S. Ebine, Chem. Commun., 782 (1970).

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