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# PHOTOCHEMICAL REARRANGEMENTS OF 2-CARBOXY-3-KETO-9-METHYL-$\Delta^{1,4}$-HEXAHYDRONAPHTHALENE

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Recently, we reported the conversion of 2-formyl-3-keto-9-methyl-$\Delta^{1,4}$-hexahydronaphthalene into a perhydroazulene derivative by irradiation in aqueous acetic acid followed by base treatment of the photo-product (1). We now have found that 2-carboxy-3-keto-9-methyl-$\Delta^{1,4}$-hexahydronaphthalene (I) is converted in high yield into 5/7-fused products on irradiation in aqueous and non-aqueous media.

The dienone acid I was prepared either by the procedure of Dreiding and Tomasewski (2) or by oxidation of the corresponding formyl compound with Jones' reagent (3). Irradiation of I at room temperature using a Hanovia 450 watt immersion light source and a Pyrex filter in aqueous acetic acid, aqueous dioxane, anhydrous dioxane, and methanol gave various mixtures of products II-V. The yields of these products and the reaction conditions are shown in Table I. The photo-products were separated by chromatography on alumina or silica gel. The dienones IV and V were difficult to separate using column chromatography and mixtures of these were analyzed by v.p.c.

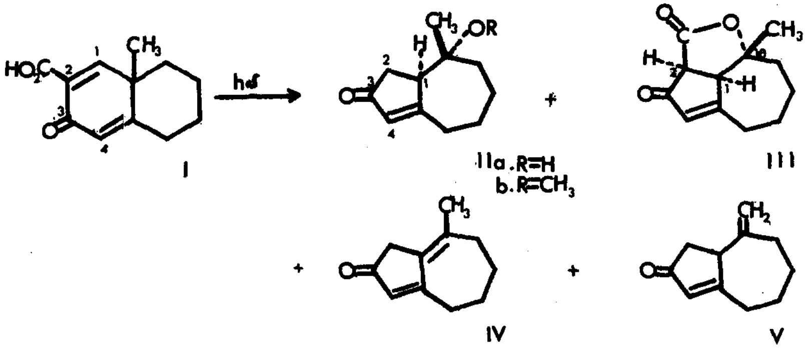


Table I. Products of Irradiation of 2-Carboxy-3-Keto-9-Methyl-$\Delta^{1,4}$-Hexahydronaphthalene (I) in Various Media[a]

| | | % Yield of Products | | | | |
|---|---|---|---|---|---|---|
| Solvent | Time(hr.) | IIa | IIb | III | IV | V |
| 45% Aqueous Acetic Acid | 2.0 | 65 | - | 6 | 5 | 7 |
| 45% Aqueous Dioxane | 2.0 | 60 | - | 12 | - | - |
| Anhydrous Dioxane | 2.0 | - | - | 16 | - | 67 |
| Anhydrous Methanol | 2.5 | - | 48 | 14 | - | 13 |

a. Irradiations conducted at room temperature employing approximately 0.3% solutions of I.

The hydroxy ketone IIa and the conjugated dienone IV were identified by comparison with authentic samples described previously (1). The exocyclic methylene compound V showed m.p. 61.0-61.5°; $\lambda_{max}^{EtOH}$ 230 mμ (ε 12,400); $\lambda_{max}^{CHCl_3}$ 5.83, 5.90, 6.06, 6.19, and 11.07 μ (cyclopentenones having no substituents at the α-vinylic position have been previously observed to give two carbonyl stretching bands (4)); $\delta_{TMS}^{CDCl_3}$ 1.18-3.06 (broad absorption, 10H), 3.56-3.82 (broad absorption, 1H, C-1H), 4.97 (s, 2H, $=CH_2$), and 5.96 p.p.m. (mult., 1H, C-4H); Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.23; H, 8.87; Molecular Weight, Calcd: 162. Found: 162 (mass spec.). The spectral and chemical properties of V are identical to those of the dienone obtained by treating IIa with thionyl chloride and pyridine (1). The methoxy ketone IIb showed m.p. 55.5-56.0°; $\lambda_{max}^{EtOH}$ 238 mμ (ε 12,600); $\lambda_{max}^{CHCl_3}$ 5.90 and 6.23 μ; $\delta_{max}^{CDCl_3}$ 0.91 (s, 3H, $CH_3\text{-}\overset{|}{\underset{|}{C}}\text{-}O$), 3.22 (s, 3H, $-OCH_3$), and 5.90 (mult., 1H, C-4H); Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.42; H, 9.40; Molecular Weight, Calcd: 194. Found: 194 (mass spec.). The stereochemical assignment of IIb is by analogy with the hydroxy ketone IIa.

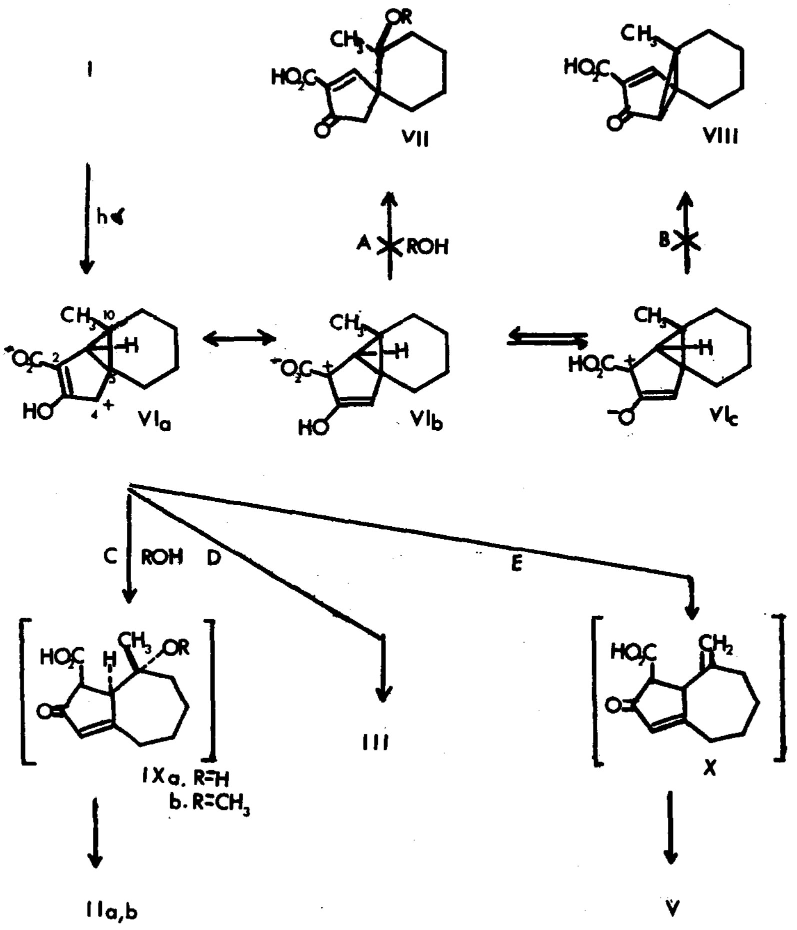
The structural assignment of the lactone III is based on spectral and chemical evidence. It showed m.p. 114.0-114.5°; $\lambda_{max}^{EtOH}$ 246 (ε 9,950) and 271 mμ (shoulder) (ε 7,380); $\lambda_{max}^{CHCl_3}$ 5.61 (γ-lactone), 5.87 (cyclopentenone), and 6.26 μ (conjugated double bond); Anal. Calcd for $C_{12}H_{14}O_3$: C, 69.89; H, 6.84. Found: C, 70.22; H, 6.73; Molecular Weight, Calcd: 206. Found: 206 (mass spec.).

The n.m.r. spectrum of III in deuteriochloroform showed a three-proton singlet at $\delta_{TMS}$ 1.05 p.p.m. for the $CH_3\text{-}\overset{|}{\underset{|}{C}}\text{-}O\text{-}$ grouping, a one-proton multiplet at $\delta_{TMS}$ 5.81 p.p.m. for the C-4 vinylic hydrogen, and an AB quartet at $\delta_{TMS}$ 3.50 and 4.07 p.p.m. ($J_{AB}$ = 7.4 cps) for the protons at C-1 and C-2. Although this point has not been definitely established, we tentatively assign the low field doublet of this quartet to the C-2 proton. The peaks of this doublet were somewhat broadened presumably because of coupling with the proton at C-4. The coupling constants of the AB quartet, indicating a dihedral angle of about 15° or less (5), are consistent with the stereochemical assignment at C-1 and C-2. On hydrolysis with aqueous sodium carbonate, acidification, and decarboxylation III yielded a mixture of IIa and IV. The conversion of III into IIa served to verify the stereochemical assignment at C-10.

The products of irradiation of cyclohexadienones have been rationalized in terms of mesoionic cyclopropyl intermediates which can either undergo internal rearrangement into lumiproducts or, in aqueous acidic media, suffer solvolytic cleavage to give spiro and/or 5/7-fused hydroxy ketones (4, 6, 7, 8). We suggest that the products of irradiation of I can best be rationalized in terms of a similar intermediate, i.e., VI, provided the electron withdrawing influence of the carboxyl group and the ability of this group to donate a proton to the ketonic carbonyl oxygen are recognized.

Because of the electron withdrawing influence of the carboxyl group, structures having a positive charge at C-2 would be expected to contribute little to the resonance hybrid VI. This would account for the fact that spiro (VII) or lumiproducts (VIII) arising from either VIb or VIc (paths A and B) were not observed on irradiation of I in any of the solvents studied.

In aqueous media and in methanol the major photo-products from I are the 5/7-fused hydroxy and methoxy ketones IIa and IIb, respectively. These products could arise from nucleophilic attack by the solvent at C-10


I
hν
OR
CH3
HO2C
VII
CH3
HO2C
VIII
A
ROH
B
CH3
10
-O2C
2
H
3
HO
4
+
VIa
CH3
-O2C
+
H
HO
VIb
CH3
HO2C
+
H
-O
VIc
C
ROH
D
E
HO2C
H
CH3
OR
O
IXa. R=H
b. R=CH3
III
HO2C
CH2
O
X
IIa,b
V

in VIa with cleavage of the 5-10 bond (path C). The β-keto acids (IXa,b) produced would be expected to decarboxylate rapidly. Solvolytic cleavage of the cyclopropane ring in a hypothetical intermediate such as VI leading to 5/7-fused products is the major photochemical reaction of cyclohexadienones having methyl substituents at C-4 in aqueous acid (4, 6, 7, 8). However, such a pathway occurs only to a minor extent on irradiation of ring A unsubstituted cyclohexadienones in this solvent (1, 4, 6, 7, 8).

The keto lactone III is a minor product of irradiation of I in all the solvents studied. Although in aqueous media this material might arise by lactonization of IXa competing with decarboxylation, its formation in anhydrous media suggests that direct attack of the C-2 carboxylate group at C-10 in VIa (path D) is involved in all solvents. Examination of models shows that considerable stretching of the 5-10 bond is required to bring the carboxylate group within bonding distance of C-10 in VIa. However, a transition state closely resembling the product in which breaking of the 5-10 bond is far ahead of formation of the new C-O bond would appear to satisfactorily explain the direct conversion of VIa into III.

Compound V, which could arise by decarboxylation of the keto acid X, was obtained on irradiation of I in all media except aqueous dioxane. It is by far the major photo-product in anhydrous dioxane. In the formation of X from VIa (path E), although a seven-membered ring transition state would be involved, it appears likely that the carboxylate group assists in the removal of a proton from the C-10 methyl group. The formation of X and hence V appears to represent the first clear-cut example of the photochemical conversion of a cyclohexadienone into a 5/7-fused system under conditions not involving solvolytic cleavage of the 5-10 bond. However, photochemical isomerization of B-nor-1-dehydrotestosterone acetate into a 5/6-fused dienone occurs in anhydrous dioxane (8).

The dienone V readily undergoes isomerization into the conjugated system IV under acidic conditions. Thus IV, obtained in low yield on irradiation of I in aqueous acetic acid, is likely to arise *via* isomerization of V during photolysis or work-up rather than as a primary photo-product.

Irradiation in aqueous acidic medium is required for the conversion of ring A unsubstituted and 4-methyl and 2-formyl substituted cyclohexadienones into 5/7-fused systems. However, the presence of the carboxyl group in I allows its facile conversion into 5/7-fused products both in nucleophilic and non-nucleophilic media. Thus cyclohexadienones having ring A substitution similar to I should be valuable intermediates in perhydroazulene synthesis.

The behavior of I and the corresponding formyl compound (1) suggests that the influence of electron withdrawing substituents at C-2 in controlling the course of rearrangement of cyclohexadienones to produce 5/7-fused systems may be general.

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