

THE PHOTOCHEMICAL BEHAVIOR OF
3-KETO-9-CARBETHOXY- $\Delta^{1,4}$ -HEXAHYDRONAPHTHALENE

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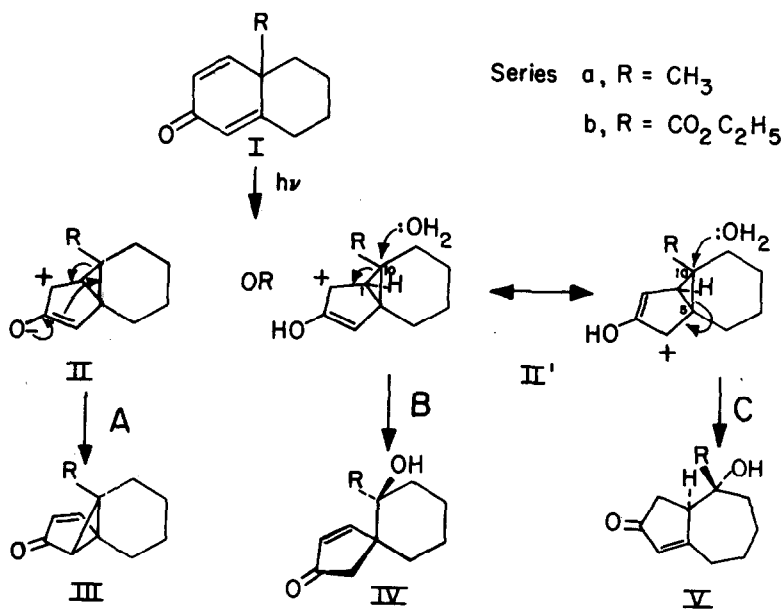
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THE extreme propensity of cross-conjugated cyclohexadienones and their cyclopropyl analogs (e.g., Ia and IIIa) for undergoing photochemical rearrangement renders these systems particularly suitable for the detailed study of photochemical processes. In connection with our investigation of the effects of substituents on the photochemical behavior of cyclohexadienones (1), we have observed several rather extraordinary properties of the carbethoxy ketones Ib and IIIb, including a rearrangement involving a formal 1,2-migration of the carbethoxy group, which offer additional insight into the nature of the light-induced rearrangements of such unsaturated ketones.

It is well established that in neutral media cyclohexadienones of type Ia undergo initial photochemical rearrangement to cyclopropyl ketones of type IIIa (1,2). In aqueous acidic media, however, the formation of type-IIIa products is greatly reduced, and hydroxy ketones of types IVa and Va are the principal photoproducts (1,3). This divergent behavior has been reconciled in terms of the intermediacy of a common cyclopropyl precursor IIa (1,4), which, as outlined in Chart I, can either undergo internal rearrangement to the cyclopropyl ketone IIIa (path A) or, in acidic media, suffer competitive nucleophilic attack to give the hydroxy ketones IVa and Va (paths B and C).

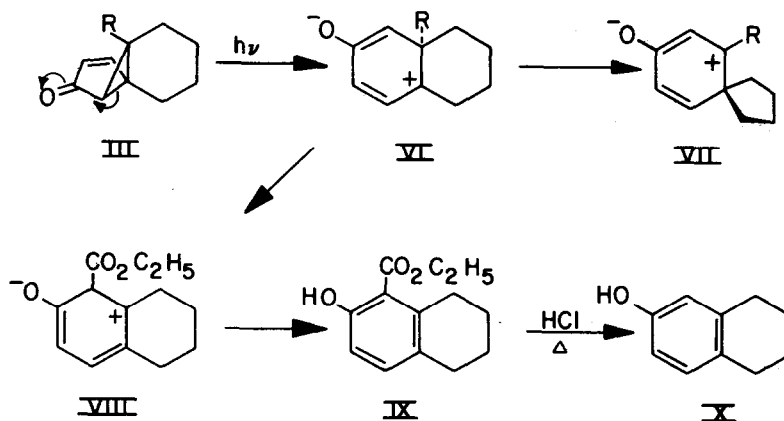
Chart I



Hence, it is noteworthy that the principal product (48-54% yield) obtained from irradiation of the carbethoxy dienone Ib (5) in either dioxane or 45% acetic acid at 2537 Å was the cyclopropyl ketone IIIb. In the latter solvent, hydroxy ketone products could be detected in no more than trace amounts. Thus, not only does path-A rearrangement still occur readily with the strongly electron-withdrawing carbethoxy substituent present at the angular position, but it occurs to the essential exclusion of rearrangement by paths B and C under conditions in which hydroxy ketone formation normally predominates. This reluctance of Ib to undergo cleavage of the two bonds bearing the carbethoxy substituent (1-10 and 5-10) provides additional support for the contention that a polar intermediate such as II, having positive character distributed

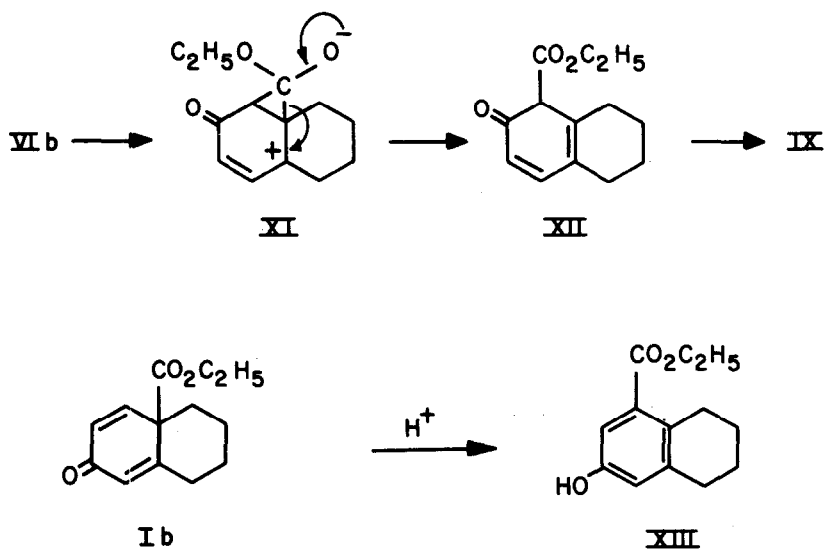
through the conjugated system of the carbon skeleton, is involved in such photochemical transformations (1,4,6).

A minor product accompanying the cyclopropyl ketone IIIb in either solvent was the tetrahydronaphthol IX. It was readily established that IX was a secondary product arising from further photochemical rearrangement of the ketone IIIb, since irradiation of a specimen of IIIb in dioxane gave IX in 90% yield. This transformation involves, at least formally, the surprising 1,2-migration of a carbethoxy group. However, some precedence for the occurrence of a direct shift of the type illustrated by VI \rightarrow VIII can be found in the recently reported acid-catalyzed rearrangement of dienone Ib to the phenol XIII (5). Alternatively, a process involving the intermediates XI and XII can be envisioned.



The rearrangement of IIIb to IX is remarkable not only because the migration of the angular carbethoxy group is so facile and free of any

competing fragmentation reactions (only trace amounts of the decarboxylation product X were formed), but also because it occurs in preference to rearrangement through the spiro intermediate VIIb. This latter pathway is the normal mode of photochemical rearrangement for cyclopropyl ketones of type III when $R = \text{CH}_3$; rearrangement via a 1,2-shift of the angular (methyl) substituent has been observed previously only in those



cases in which the formation of a five-membered B ring is sterically prohibited (1). It is not clear, however, whether the preferred migration by the carboxy group in this case arises from (a) an inherently greater migratory aptitude of that group relative to methylene or (b) a destabilization of the spiro intermediate VIIb by the presence of the electron-withdrawing carboxy substituent on the electron-deficient A ring. Additional work designed to clarify these points is in progress.

Characterization of Products. - The cyclopropyl ketone IIIb (7) exhibited the expected infrared absorption at 5.76 (ester carbonyl), 5.84 (cyclopentenone carbonyl) and 6.34 μ (double bond) and ultraviolet absorption at 215 (ϵ 4,200) and 252 m μ (ϵ 1,500). The olefinic protons of IIIb appeared in the n.m.r. spectrum as an AB quartet consisting of doublets centered at 2.72 and 4.26 τ ($J_{AB} = 5.5$ c.p.s.), the latter of which was further split by coupling with the tertiary cyclopropyl proton ($J_{AX} = 0.8$ c.p.s.). Finally, IIIb formed a dihydro derivative, b.p. 112-114° at 0.3 mm., which displayed the strong, broad absorption at 5.80 μ which would be expected for a superposition of the characteristic absorption bands of the bicyclo[3.1.0]hexan-2-one system and an ester group. By analogy with the formation of similar cyclopropyl ketones under these conditions and the similarity to their spectral data (1,2), the structure and stereochemistry IIIb is assigned to this photoproduct.

The secondary photoproduct IX, m.p. 34.5-35°, exhibited the appropriate carbonyl absorption for an ester of an aromatic acid at 6.04 μ . Both the infrared (12.14 μ) and n.m.r. spectra (doublets at 2.86 and 3.20 τ , $J_{AB} = 8$ c.p.s.) revealed that the two aromatic protons are adjacent to each other and that the carbethoxy and hydroxyl groups thus bear either an ortho or a para relationship. Since the n.m.r. spectrum further revealed that the hydroxyl proton is intramolecularly hydrogen-bonded (singlet at -0.87 τ), an unequivocal choice in favor of the ortho substitution pattern was possible. This was corroborated when decarboxylation of the photoproduct gave 5,6,7,8-tetrahydro-2-naphthol (X) in 67% yield.

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- (7) Satisfactory analytical data have been obtained for all new compounds reported here.