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PHOTODIHYDRODIMERIZATION OF SOME CYCLOPROPYL CONJUGATED 1,2-DIKETONES

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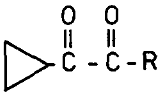
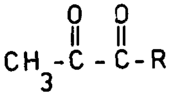
We have studied the behaviour of three cyclopropyl conjugated 1,2-diketones (I a, b, and c) [1] in isopropanol upon irradiation with a Philips SP 500 W mercury lamp (with 436 nm as the most intense line). For comparison we extended this study to three non-cyclopropyl containing 1,2-diketones, viz. biacetyl (Id), 1-phenyl-1,2-propanedione (I e) and benzil (I f).

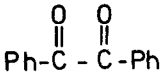


I a R = cyclopropyl
b = methyl
c = phenyl



$CH_3-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-R$

I d R = methyl
e = phenyl



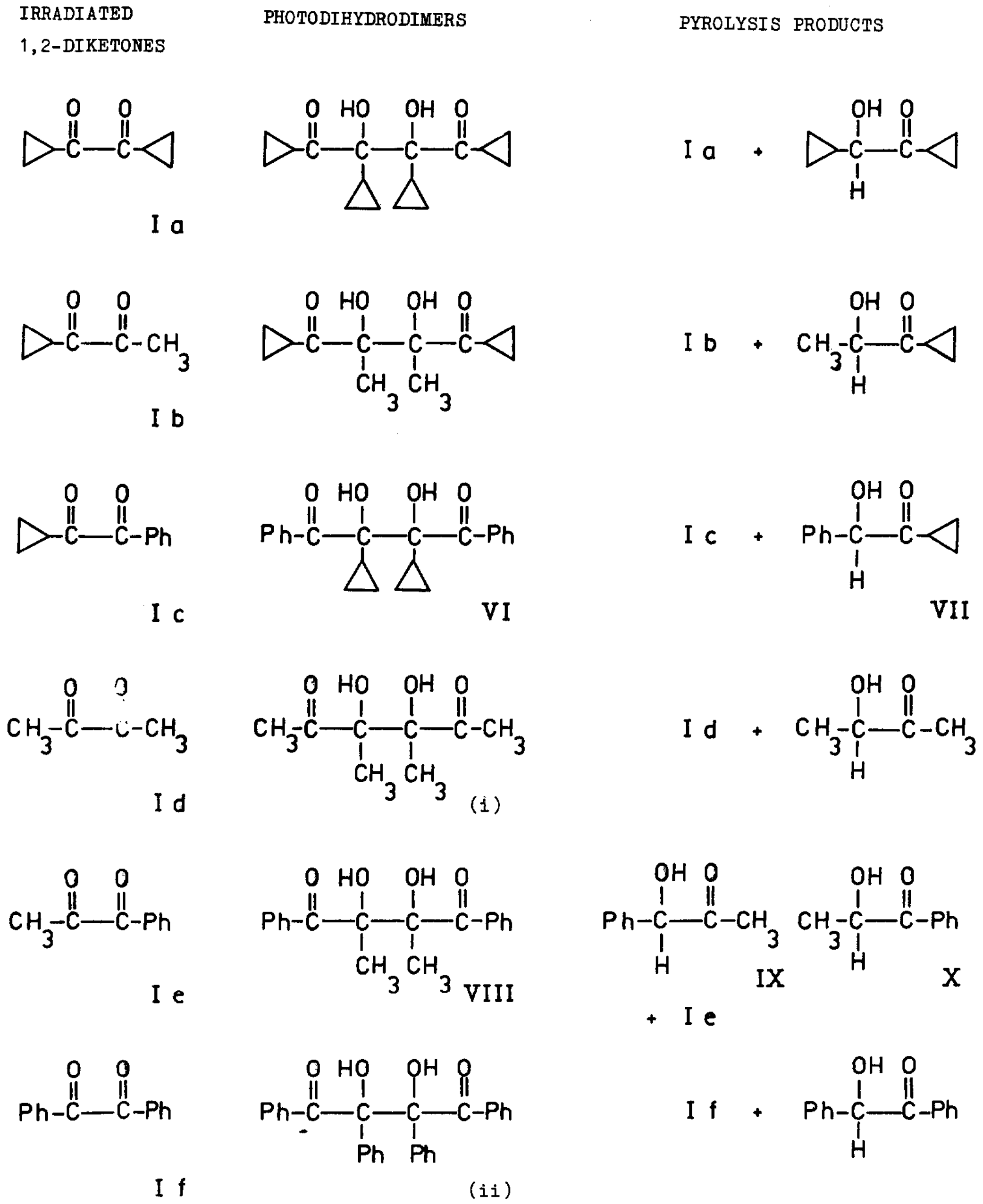
$Ph-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-Ph$

I f

All the photolysis experiments were performed in a tap-water cooled pyrex vessel with nitrogen inlet. The diketone solutions (0.1 molar) in isopropanol were irradiated until the yellow colour of the 1,2-diketones had completely disappeared (within 20 minutes). After careful removal of the solvent under diminished pressure, white crystalline mixtures of diastereomeric photodihydrodimers were obtained in a nearly quantitative yield. The diastereoisomers were separated by fractional recrystallization (mostly from petroleum ether 40-60). The products were identified on the basis of their infra-red, proton magnetic resonance and mass spectra.

Heating of the photoproducts for a few hours at 150° under nitrogen led to their complete decomposition. The pyrolysis products were isolated by preparative gas chromatography and identified by means of infra-red and proton magnetic resonance spectrometry. The table lists the photodihydrodimers we obtained, as well as their pyrolysis products.

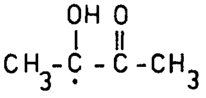
The first step in the photochemical process is abstraction of hydrogen from isopropanol by the excited 1,2-diketone with formation of a semidione radical.[2] Evidence for the presence of this type of radical has been obtained from esr studies of irradiated



(i) Cf. W.G.Bentrude,K.R.Darnall, Chem.Comm. 1968, 810.

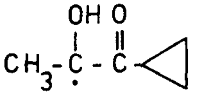
(ii) Cf. H.Klinger, Ber. 19, 1862 (1886)

1,2-diketones in isopropanol.[3,4] Upon irradiating dilute solutions of biacetyl (I d) in mixtures of isopropanol/pentane or isopropanol/benzene in the cavity of a Varian E-3 EPR spectrometer, we observed the dimethylsemidione radical (II) (cf. [3]). Of the other five 1,2-diketones studied, we observed a semidione radical (III) only from (I b). Upon irradiating dicyclopropylethanedione (I a), we detected a very weak singlet esr signal which will be discussed later on.



$CH_3-\overset{OH}{\underset{\bullet}{C}}-\overset{O}{\overset{\|}{C}}-CH_3$

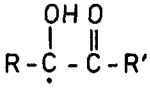
(II)



(III)

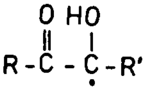
The esr spectra of the semidione radicals (II) and (III) exhibit a predominant quartet splitting due to the methyl hydrogen atoms ($a_{\alpha\text{-}CH_3}$ = 12.6 gauss). Furthermore, in the case of radical (II) each line is split in a nearly perfect quintet by coupling of the hydrogen atoms of the other methyl group and the hydroxyl group (a = 2.1 gauss). In the case of radical (III) there is only coupling of the hydroxyl hydrogen atom (a = 2.1 gauss). Coupling of the methine hydrogen atom of the cyclopropyl group was not observed. This is due to the specific orientation of the three-membered ring with respect to the carbonyl group.[5] In this so-called "bisected form", the methine hydrogen atom of the cyclopropyl group lies in the nodal plane of the π-system. The structures of the photoproducts (see table) illustrate that the detected semidione radicals are indeed the radicals involved in the dimerization process.

In principle two different semidione radicals may be formed when the excited state of an unsymmetrical 1,2-diketone abstracts a hydrogen atom from the solvent (viz. IV and V):



$R-\overset{OH}{\underset{\bullet}{C}}-\overset{O}{\overset{\|}{C}}-R'$

(IV)



$R-\overset{O}{\overset{\|}{C}}-\overset{HO}{\underset{\bullet}{C}}-R'$

(V)

The ease of formation of the one semidione radical as compared with the other is reflected by the composition of the products formed from these radicals, except when there is a rapid tautomerization of (IV) and (V). Zeldes and Livingston [3], as well as Pritchett [6] have demonstrated by esr the tautomerization of dimethylsemidione radicals (IV and V; R = R' = methyl). In our opinion, these tautomerization processes are relevant for the explanation of some of our photolysis and pyrolysis experiments (see table).

On pyrolysis of the six listed photodihydrodimers, a mixture of the "original" 1,2-diketone and one or two α-hydroxyketones was obtained. The formation of these compounds can be explained in terms of a homolytic cleavage of the central carbon-carbon bond of the dimer with formation of two semidione radicals, followed by hydrogen atom transfer from one semidione radical to the other (disproportionation).

The pyrolysis of (VI) leads to the unexpected α-hydroxyketone (VII) (see table), whereas the pyrolysis of (VIII) leads to the formation of two α-hydroxyketones, (IX) and (X). The formation of these unexpected products is the result of tautomerization of the semidione radical preceding the disproportionation.

An alternative explanation, viz. isomerization of the α-hydroxyketone after the disproportionation, seems less likely, as it does not explain all the pyrolysis results. Experiments to decide whether the isomerization is a relevant process under our conditions, are in progress.

It is remarkable that no ring-opened products are isolated upon irradiating cyclopropyl conjugated 1,2-diketones in isopropanol, since Marsh, Pitts, Schaffner, and Tuinman [7] have shown that the irradiation of dicyclopropyl ketone in isopropanol leads to the exclusive formation of propyl cyclopropyl ketone. This result means that the presumed α-hydroxydicyclopropylcarbinyl radical intermediate is not stable and leads to ring-opening of one of the three-membered rings. Upon irradiation of dicyclopropylethanedione (I a) in isopropanol, one expects a similar radical. The absence of ring-opening in that case is explained by the reduced radical character α to the cyclopropyl ring as result of the conjugative stabilization effect of the adjacent carbonyl group. We believe that in addition there is a rapid tautomerization of the semidione radicals (IV and V; R = R' = cyclopropyl). The observation of a very weak singlet esr signal upon irradiation of dicyclopropylethanedione (I a) in isopropanol/pentane seems to support this assumption. This singlet signal can be interpreted as being the result of a rapid (on the esr time scale) tautomerization of the dicyclopropylsemidione radical.

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