

The results are given of a study of the photoreaction of osthole in chloroform and acetophenone. It has been shown that when it is irradiated in the latter solvent the cyclization characteristic for coumarins takes place at the double bonds both in the 3,4- position of the coumarin ring and in the side chain, leading to the formation of cyclobutane structures.

We have previously [1] shown experimentally that on irradiation with visible light in chloroform 6-isopentenyl-7-methoxycoumarin [suberosin (I)] undergoes photooxidation, as a result of which lophopterol (II) and suberenol (III) are formed, while under the same conditions a structural isomer of (I) 8-isopentenyl-7-methoxycoumarin [osthole (IV)] does not take part in a photoreaction. Later, (III) was also obtained by the irradiation of (I) in pyridine by other workers [2]. However, a report has appeared in the press [3] according to which when (IV) is irradiated in chloroform with sunlight photooxidation does in fact take place, with the formation of merancin (V), isomerancin (VI), and merancin hydrate (VII), compounds (V-VII) having been identified by thin-layer chromatography (TLC) and gas-liquid chromatography (GLC).

In view of this, we have again performed this reaction under the conditions described by Kuznetsova [3]. The course of the reaction was checked by TLC on Silufol plates and by NMR spectroscopy with Fourier transformation. The results of the investigation showed that, as previously [1], during a month no changes whatever took place in osthole (IV) not only under the action of visible light but also on irradiation with UV light having λ_{254} and 365 nm. Consequently, when chloroform is used as sensitizer (IV) undergoes no photooxidation and the results given by Kuznetsova [3] do not correspond to the truth. We arrived at this conclusion on the basis of facts given in the literature [4] and the results of our own investigations, which showed that the GLC method used by Kuznetsova [3] is not objective for the identification of coumarin compounds, since during this process various thermal transformations are possible, all the more because in her work [3] chromatography was carried out at the very high temperature of 256°C [the melting point of (IV) being 82°C, of (V) 66°C, and of (VI) 101°C]. Consequently, at the present time the GLC method is hardly used in investigations of coumarins. Furthermore, the formation of (VII) [the hydrolysis of the epoxy group in (V)] during a photoreaction does not appear possible on the basis of existing laws of organic photoreactions [5].

The investigation that we have performed has established that out of the sensitizer solvents tested the most suitable for the photoreaction of (IV) are acetophenone and acetonitrile, since in them the reaction takes place fairly fast and the compounds formed are determined quantitatively. For example, when (IV) was irradiated with UV light at λ_{254} nm in acetophenone for 12 h at least three substances (VIII-X) with the same chemical composition, $C_{30}H_{28}O_6$, were formed. The IR spectra of these compounds lacked the absorption band of hydroxy groups and their structures were unambiguously determined with the aid of PMR spectroscopy.

Thus, in the PMR spectrum of (VIII) (Fig. 1) in the region of aromatic protons there are the signals of the protons of a 7,8-disubstituted coumarin ring, and in the region of aliphatic protons it is possible to see the signals of the protons of four methyl groups on quaternary carbon atoms (singlets at 1.08 and 1.16 ppm, 6 H each), of two cyclic methine protons (multiplet, 1.60-1.94 ppm, 2 H), of two methylene groups attached to aromatic rings (quartet, 3.06 ppm, $J_1 = 12$ Hz, $J_2 = 6$ Hz, 4 H), and of methoxy groups (singlet, 3.92 ppm, 6 H). These facts are in complete harmony with structure (VIII).

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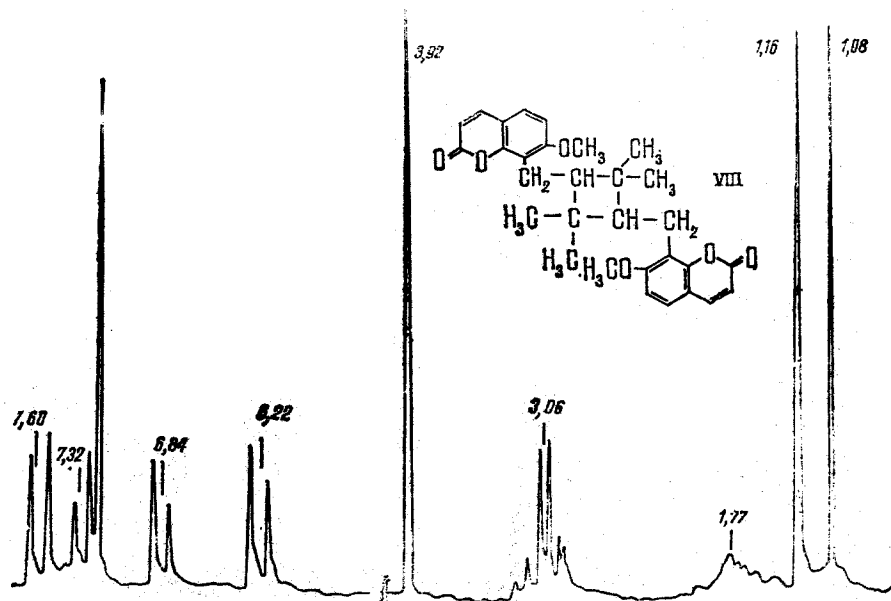


Fig. 1. PMR spectrum of substance (VIII).

In the PMR spectrum of (IX) (Fig. 2), the picture is the opposite, i.e., the signals observed in the strong field are due to the protons of two methoxy and two isopentenyl groups and in the weak field only the signals of H-3 and H-4 are lacking.

Thus, the most correct structure for the compound under investigation is (IX).

The signals of the cyclic methine protons in (IX) appear in the 2.19-2.42 ppm interval (multiplet, 4 H).

The study of the structure of (X) is continuing. Thus, it may be concluded that the irradiation of (IV) in acetophenone with UV light leads to the photocyclization at the double bonds that is characteristic for coumarins, both in the 3,4-positions of the coumarin ring and in the side chain, leading to the formation of cyclobutane structures.

EXPERIMENTAL

The IR spectra were taken on a UR-20 spectrometer (in paraffin oil) and the PMR spectra on a HX-90 spectrometer (in CDCl_3 , 0 - TMS), melting points were determined on a Kofler block. The purity of the substances obtained was confirmed on Silufol plates in the benzene-acetone (10:1) system. The elementary analyses of the compounds under investigation corresponded to the calculated figures.

Photoreaction of Osthole (IV) in Chloroform. In quartz glass and ordinary glass vessels, 1.0 g of osthole was dissolved in 5 ml of dry chloroform, and they were kept in the light for a month. During this time no changes whatever took place in the osthole, since after evaporation of the solvent the residue obtained corresponded to the initial osthole in its IR and PMR spectra. Similar results were obtained when the same sample was irradiated with UV light having λ 254 and 365 nm.

Photoreaction of Osthole (IV) in Acetophenone. In a quartz-glass vessel, 1.0 g of (IV) was dissolved in 5 ml of acetophenone and the solution was irradiated with UV light having λ 254 nm for 12 h. In this process the solution acquired a dark brown color. Then the reaction mixture was concentrated in vacuum and the residue, which consisted of four substances, was separated preparatively under the conditions described above. This gave: the initial substance (IV), $\text{C}_{15}\text{H}_{16}\text{O}_3$, mp 81-82°C, R_f 0.74 (pale blue), (VIII), $\text{C}_{30}\text{H}_{28}\text{O}_6$, mp 151-152°C, R_f 0.03 (pale blue), (IX), $\text{C}_{30}\text{H}_{28}\text{O}_6$, mp 113-115°C, R_f 0.06 (dark), and (X), $\text{C}_{30}\text{H}_{28}\text{O}_6$, R_f 0.10 (dark). The IR spectra of the residue investigated and of the compounds isolated in the individual state lacked the absorption bands of hydroxy groups.

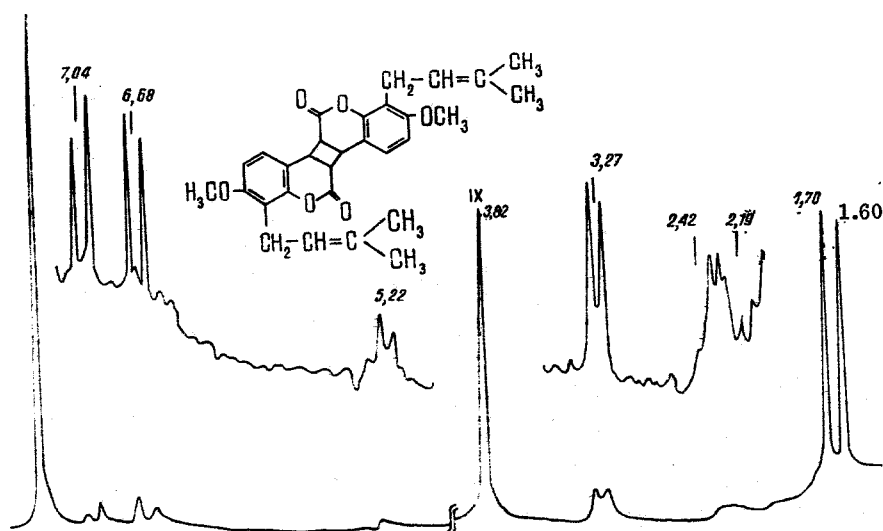


Fig. 2. PMR spectrum of substance (IX).

SUMMARY

The photoreaction of osthole in acetophenone has been studied, and it has been established that when osthole is irradiated with UV light photocyclization takes place not only at the double bond in the 3,4-positions but also in the side chain, which leads to the formation of cyclobutane structures.

LITERATURE CITED

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