

PHOTOCHEMISTRY OF β -HYDROXY- γ -PYRONE.

A NEW SYNTHESIS OF 3-METHYLCYCLOPENT-2-EN-2-OL-1-ONE FROM MALTOL

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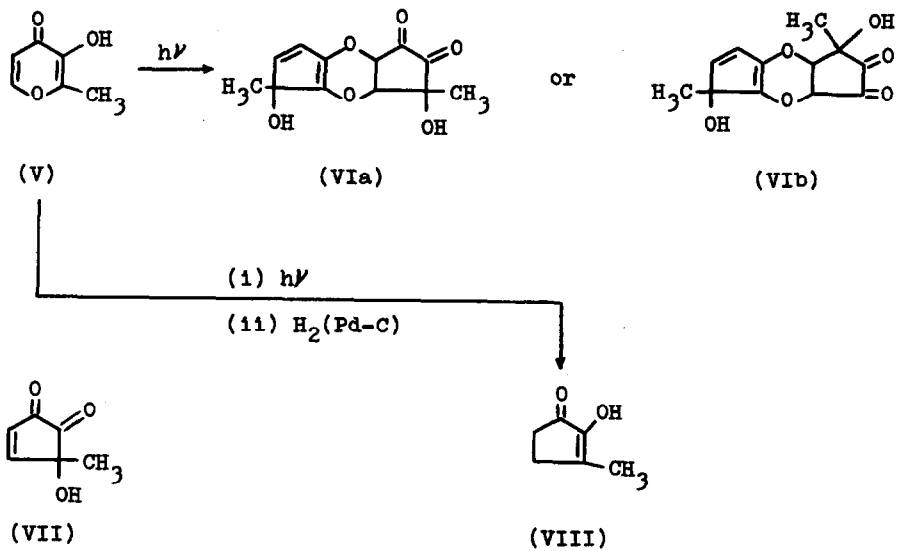
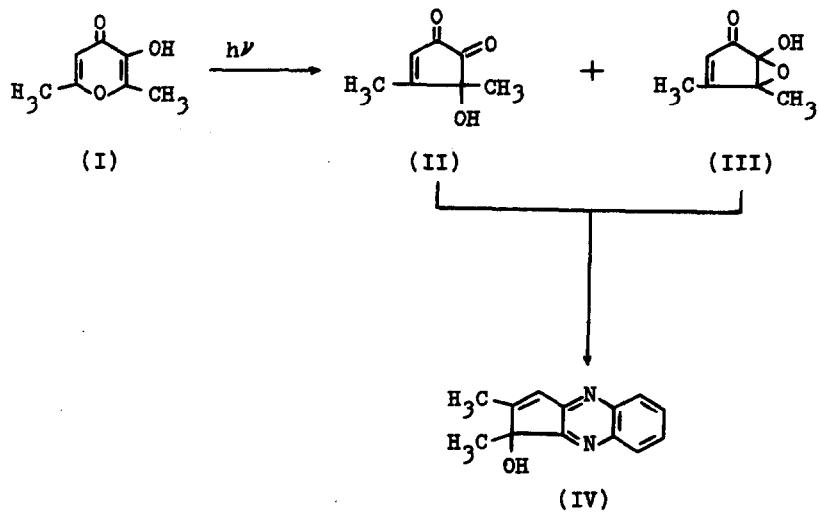
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While photorearrangements of cross-conjugated cyclic dienones are well known¹, the photochemistry of γ -pyrone is limited in its utility since a complex rearrangement was encountered in addition to dimerization.² This complexity depends upon the nature of an intermediate zwitterion, whose intermolecular nucleophilic trapping was achieved in the cyclohexadienone system by Schuster et al.³ This evidence suggests that intramolecular quenching of the zwitterion generated from γ -pyrone by photochemistry would give a clear-cut product. Thus a hydroxyl group situated at the β -position in a γ -pyrone derivative would be suitable for effecting quenching of the zwitterionic intermediate. In this respect, Matura's recent report⁴ on the photochemistry of 3-hydroxyflavones is very interesting. We now wish to report the photochemistry of β -hydroxy- γ -pyrone and its successful utilization for a synthesis of a natural product.

A one percent solution of 2,6-dimethyl-3-hydroxy-4H-pyran-4-one (I)⁵ in methanol was irradiated with an ultraviolet lamp (Hanovia, 450 W) through a Corex filter under nitrogen for 2.5 hr to give an oil after usual work-up. After standing for several days the oil afforded a crystalline material which was separated from an oily residue by filtration. The crystals obtained above (26.5% yield) were concluded to be a mixture of an α -diketone II and epoxy-hemiketal III (1:1 ratio) on the basis of the following spectroscopic data: mp 150-165°C (from ethyl acetate), $\nu_{\max}^{\text{Nujol}}$ 3520, 3400, 1720, 1615 and 1120 cm^{-1} , nmr (DMSO- d_6)

§ 1.23 (3H, s, CH₃), 1.40 (3H, s, CH₃) 2.02 (3H, d, J=1.5 Hz, CH₃), 2.08 (3H, d, J=1.5 Hz, CH₃), 5.05 (1H, s, OH), 6.00 (2H, m, olefinic hydrogens), and 7.55 (1H, s, OH). These structures of II and III were further confirmed by chemical transformation. Treatment of this crystalline mixture with o-phenylenediamine gave only one crystalline quinoxaline derivative IV in quantitative yield, mp 158.5-159°C, $\nu_{\max}^{\text{Nujol}}$ 3310, 1621 and 1600 cm⁻¹, nmr (CDCl₃) § 1.60 (3H, s, CH₃), 2.15 (3H, d, J=1.5 Hz, CH₃), 4.80 (1H, s, OH), 6.50 (1H, q, J=1.5 Hz, CH=C), and 7.46-8.10 (4H, m, aromatic hydrogens). Compound IV was obtained in 49% yield on treatment of the crude photoproduct from I with o-phenylenediamine. The epoxy-hemiketal III has quite an unusual structure, which would only be probable in the case of a 3-hydroxy-1,2-diketone system.

Analogously, 3-hydroxy-2-methyl-4H-pyran-4-one (V)(maltol) was irradiated, and the crude photoproduct was purified by preparative tlc to afford an oil and a crystalline compound, mp, 186-187°C, $\nu_{\max}^{\text{Nujol}}$ 3480, 3300, 1790, and 1740 cm⁻¹ mass spectrum m/e 252(M⁺), nmr (100 MHz, DMSO-d₆) § 1.44 (3H, s), 1.47 (3H, s), 4.76 (1H, d, J=3.5 Hz), 4.82 (1H, d, J=3.5 Hz), 5.29 (1H, s, OH), 5.73 (1H, d, J=6.0 Hz), 5.99 (1H, d, J=6.0 Hz), and 6.59 (1H, s, OH). These data strongly suggested the structure of the crystalline photoproduct should be described as VIa or VIb, which would arise from the normal photoproduct VII by dimerization. This kind of dimerization was already known in the photochemical reaction of an α -diketone derivative with an olefin.⁷ The oily part of the above reaction product was hard to work up due to its instability. Therefore, an irradiated methanolic solution of maltol (V) was hydrogenated over palladium on carbon until two moles of hydrogen were absorbed. Purification by preparative tlc gave 3-methylcyclopent-2-en-2-ol-1-one (VIII), mp 105-106°C, in 13% yield. Compound VIII obtained here was identical with the authentic sample⁸ in all respects. Thus, the natural flavoring component VIII isolated from coffee⁹ was synthesized in only 2 steps from maltol (V), which is also a natural product.



References

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