

PHOTOINDUCED REACTIONS. XXIII. A NOVEL PHOTOREARRANGEMENT

OF SANTONIN IN THE SOLID STATE¹

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(Received in Japan 20 July 1968; received in UK for publication 6 August 1968)

The photoreactions of santonin (1), which gave various types of products depending upon conditions employed, have been the topic of much work.^{2,3} We wish to report a novel photorearrangement of 1 to a cyclopentadienone 11 followed by spontaneous dimerization of 11. Irradiation of crystals of santonin in the solid state afforded three dimers C₃₀H₃₆O₆,⁴ A (mp 231-232°), B (mp 218°), and C (mp > 300°), in addition to lumisantonin (9) and a new photoisomer (mp 171-173°) of santonin.^{5,6} Further irradiation of dimer A in ethanol gave dimer C. From the following chemical and spectral evidences structure 2 was assigned for dimer A and structure 3 for dimer C.

Dimer A shows the parent peak at m/e 492 in the mass spectrum and no olefinic proton in the NMR spectrum. A UV maximum at 243.5 mμ (ε 9600) and an IR band at 1695 cm⁻¹ suggest the presence of an α,β-disubstituted 2-cyclopentenone, whereas dimer C shows only end UV absorption and a broad IR band around 1760 cm⁻¹. The NMR spectrum of dimer A exhibits, in addition to signals indicating the presence of two γ-lactone moieties similar to that of 1, two singlets (2- and 2'-H, τ 6.43 and 7.77) and four methyl signals at τ 8.15 (4'-Me, d, J = 1.5 Hz), 8.42 (4-Me, s), and 8.76 and 8.84 (10- and 10'-Me, d, J = 6 Hz). On the other hand, the NMR spectrum of dimer C indicates that the olefinic methyl (4'-Me) signal of dimer A is replaced by a tertiary methyl signal. Thus, intramolecular C₄-photocycloaddition⁷ can account for the formation of dimer C from dimer A. Catalytic hydrogenation (Pd on charcoal) or NaBH₄-reduction of dimer A resulted in selective reduction of the saturated carbonyl yielding an alcohol 4a (mp 240-242°). In the NMR spectrum of its acetate (4b), a newly formed 3-proton (τ 5.62, d) was found by decoupling experiments to couple with 2-proton (τ 6.69, d, J = 2 Hz).

Pyrolysis of dimer A at 250° caused decarbonylation to yield a compound C₂₉H₃₆O₅ [mp 278-280°; ν_{max}^{KBr} 1780, 1710, and 1595 cm⁻¹; λ_{max}^{EtOH} 216 mμ (ε 24100), 254 (14600), and 297 (1350)].

Its NMR spectrum exhibits five Me-CH₂ groups (8.59 (J = 7.0 Hz), 8.65 (6.0), 8.76 (6.2), 8.80 (7.0), and 8.87 (7.0) , a highly deshielded aromatic methyl (7.25), and an aromatic proton (2.61). Structure 5 was tentatively given for this compound. Similar aromatization reactions are known for dimeric cyclopentadienones.⁸ Treatment of dimer A with methanolic hydrogen chloride afforded a dehydro-ester C₃₁H₃₈O₆ [mp 198-202°; λ_{max}^{EtOH} 241.3 mμ (ε 15400), 269 (5820), 314 (1960); ν_{max}^{KBr} 1780, 1735, 1700, and 1630 cm⁻¹; NMR (CDCl₂), a broad singlet at 7.99 (1H, =CH-), singlets at 6.39 (3H, COOMe) and 8.32 (3H, =C-Me), and other signals similar to dimer A]. Structure 6 is well consistent with the spectral properties. The facile formation of 6 suggests that the C-O bond at 6-position and the C-H bond at 10-position in dimer A hold an anti-parallel conformation through the 1,5-double bond, namely dimer A has 10β-methyl configuration.

Structure 2 without assignment of stereochemistry at 1-, 2-, 1'- and 2'-positions was confirmed by a synthesis of dimer A. Bromination of compound 12⁹ with N-bromosuccinimide followed by dehydrobromination of the 1-bromo derivative 13 yielded dimer A.

We can now formulate a three-dimensional structure 2 or 2a for dimer A.¹⁰ The circular dichromism (CD) spectrum of dimer A in ethanol exhibits a negative CD maximum ([θ]₃₃₉ -6900) in the n,π*-region. Its dihydro-derivative 4a also show a negative CD maximum ([θ]₃₄₁ -2920) indicating that the sign of the CD maximum associated with the 2-cyclopentenone grouping should be negative. Considering the CD data available for 2-cyclopentenones with a fused ring system,¹¹ it may be reasonable to assume that dimer A possesses structure 2. On the other hand, the optical rotatory dispersion curve of dimer C exhibits a negative Cotton effect ([φ]₃₃₃ -47750). A simple application of the octant rule to the 3'-carbonyl with structure 3 may predict a negative effect which is due to a significant contribution of 1', 10'-bond.¹² From the above results it led us to propose that dimer A may be more favorably represented by structure 2.

It is generally accepted² that santonin (1) undergoes rearrangement to lumisantonin (9) via an intermediate 8 which is formed by rebonding from the excited triplet state 7a as shown in Chart 1 (path a). The formation of cyclopentadienone 11, the precursor of dimer A (2), could be rationalized by migration of a hydrogen atom at 1-position of an intermediate 10 which may be formed from either 7b or 8. Cohen and Schmidt and coworkers investigated photochemical reactions of certain organic compounds in the solid state, and they concluded that reaction in the solid state occurs with a minimum amount of atomic movement.¹³ The highly

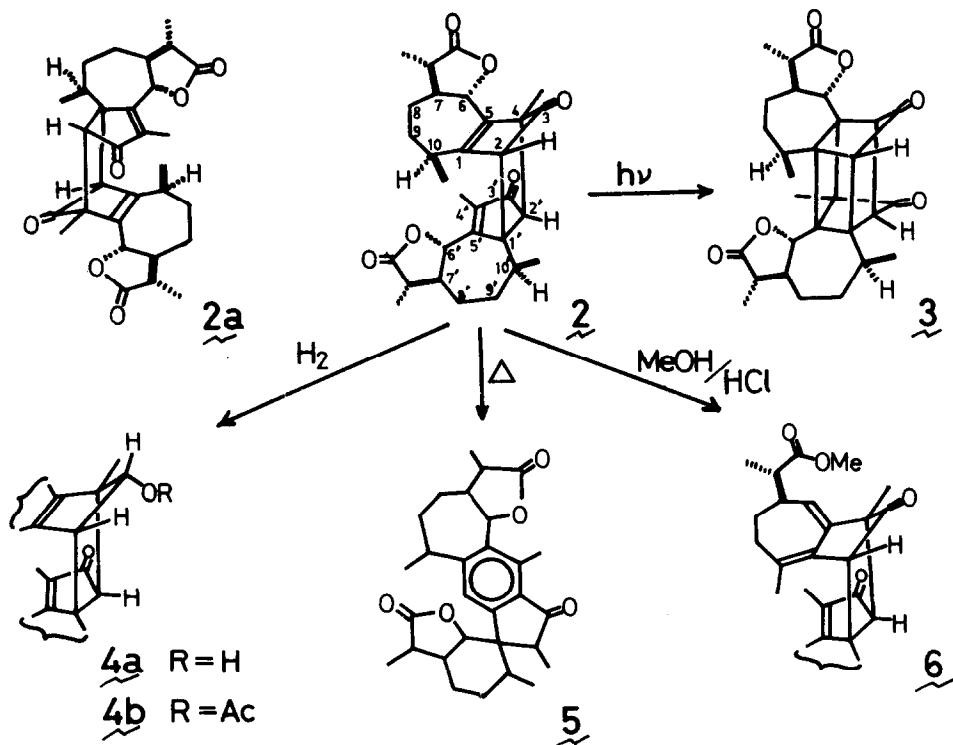
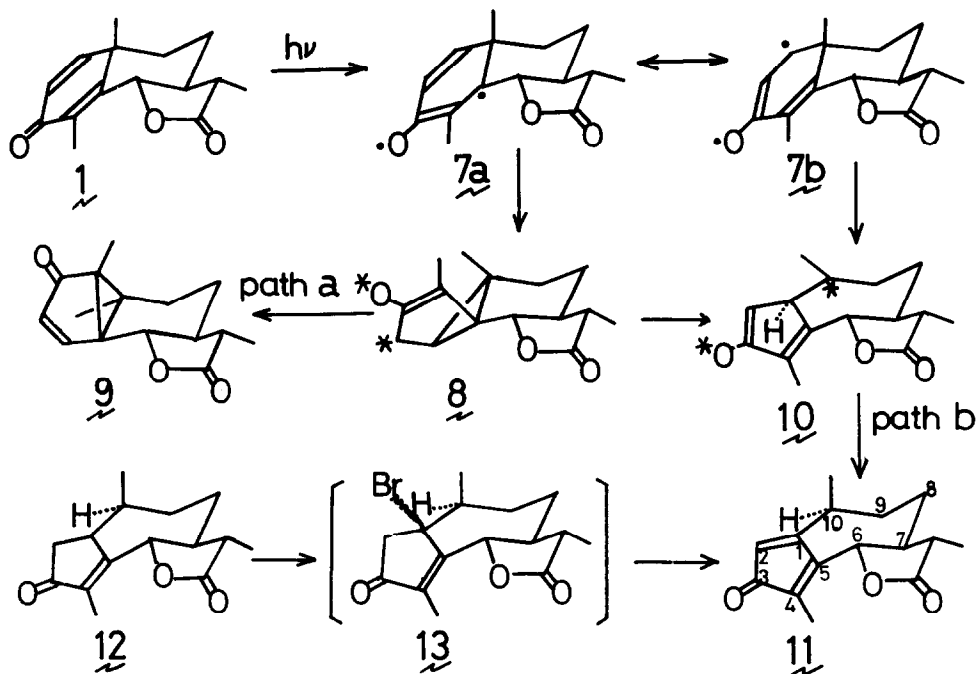


Chart 1 * = . or + . -



selective transformation of santonin to 11 predominant over lumisantonin formation may be interpreted by considering that path a needs larger movements in the geometry of santonin than path b.

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3. M. I. Geryaev and R. N. Sazonova, Izvest. Akad. Nauk Kazokh. SSR., Ser. Khim., No. 2, 75 (1957); Chem. Abstr., 52, 11590 (1958), have reported photochemical behavior of santonin in the solid state but no detailed account of the products are given.
4. Satisfactory microanalyses and spectral data were obtained for all new compounds, in addition to those described in this communication.
5. In a typical run, irradiation of powdered crystals (recrystallized from methanol) of santonin (125 g) with a high-pressure mercury lamp through Pyrex, followed by fractionations of the resulted yellow-colored material by crystallization and chromatography gave the products. The recovered santonin was repeatedly treated as above. Thus, dimer A (12 g), dimer B (0.15 g), dimer C (2.5 g), lumisantonin (0.50 g), and a new photoisomer of santonin (0.8 g) were obtained.
6. The structure of the new photoisomer is under investigation.
7. For examples of the intramolecular cycloaddition of a cyclopentadienone dimer, see P. E. Eaton and T. W. Cole, Jr., J. Am. Chem. Soc., 86, 962, 3157 (1964).
8. M. A. Ogliaruso, M. G. Romanelli, and E. I. Becker, Chem. Revs., 65, 261 (1965).
9. G. Büchi, J. M. Kauffman, and H. J. E. Loewenthal, J. Am. Chem. Soc., 88, 3403 (1966).
10. Eight stereoisomers are possible for the structure of dimers which can be derived from cyclopentadienone 11. Six structures other than 2 and 2a were eliminated from the fact that two protons at 2- and 2'-positions appear as a set of singlets in the NMR spectrum of dimer A, and that irradiation of dimer A gives the cage dimer C. Dimer B, which shows an AB-type quartet at τ 6.72 and 7.25 ($J = 5$ Hz, 1- and 1'-protons) in its NMR spectrum, appears to be a dimer which is formed by 1,4'- and 2,2'-bond formations from 11. The total structure of dimer B remains to be elucidated.
11. G. Snatzke and Ch. Tamm, Helv. Chim. Acta, 50, 1618 (1967).
12. An octant projection from the 3-carbonyl group shows that this carbonyl absorption may not significantly contribute to the Cotton effect because of its nearly symmetrical projection diagram. However, an anomalously large amplitude in the Cotton effect of dimer C remains to be further studied. The authors are indebted to Dr. Kaoru Kuriyama of Shionogi Research Laboratory for discussions on the CD and ORD results.
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