Tetrahedron Letters No. 21, pp. 939-943, 1962. Pergamon Press Ltd. Printed in Great Britain.

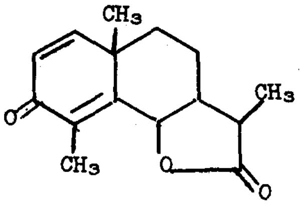
ULTRAVIOLET IRRADIATION OF 2,4-DIMETHYL-4-DICHLOROMETHYL-CYCLOHEXA-2,5-DIENONE-1

E.E. van Tamelen, K. Kirk and G. Brieger

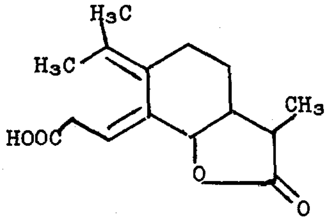
Department of Chemistry, University of Wisconsin, Madison 6, Wisconsin

(Received 23 July 1962)

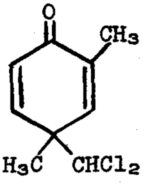
DISCOVERY of the profound molecular changes involved in the photochemical conversion of santonin (I) to photosantonic acid (II),[1] the structure of which was established in this Laboratory,[2] prompted broader investigation of carboxylic acid production by ultraviolet irradiation of cross-conjugated dienones. The abnormal Reimer-Tiemann reaction product III represents an interesting variant; and we have now found that this dienone is transformed



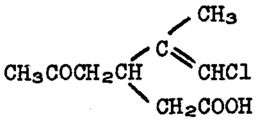
I



II



III



IV

[1a] F. Radt (Editor), Elsevier's Encyclopedia of Organic Chemistry Series III, Vol. 12B, p. 3733. Elsevier, Amsterdam (1953); [b] J. Simonsen and D.H.R. Barton, The Terpenes (2nd Ed.), Vol. III, p. 249. Cambridge University Press (1952).

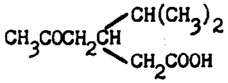
[2] E.E. van Tamelen, S.H. Levin, G. Brenner, J. Wolinsky and P.E. Aldrich, J. Amer. Chem. Soc. 80, 501 (1958); 81, 1666 (1959).

on photolysis to the acid IV, obviously arising from a reaction path which is, in respect to novelty and complexity, the equal of the aforementioned prototype.

After irradiation (Hanovia Type L lamp) of a solution of dienone III in 1:1 acetic acid-water for 24 hr, a small yield of acidic transformation product was isolated by evaporation, extraction with sodium bicarbonate, followed by acidification with mineral acid and ether extraction. Recrystallization from ether afforded the pure photo acid (m.p. 108-109°), analysis of which indicated the molecular formula $C_9H_{13}O_3Cl$ (Found: C, 52.94; H, 6.43; Cl, 17.39. Calc.: C, 52.81; H, 6.36; Cl, 17.36).

The ultraviolet spectrum $\lambda_{max}^{alc.}$ 278 mμ (ε = 30), demonstrated the presence of a non-conjugated ketonic carbonyl group, the nature of which was further revealed by a positive iodoform test. Alcoholic silver nitrate had no action on the photoacid. In the infrared ($CHCl_3$) broad absorption in the 3-4 μ and 5.80-5.90 μ regions was observed, while a weak, but sharp peak at 6.13 μ suggested olefinic bonding.

Two moles. of hydrogen were absorbed on reduction over 10 per cent palladium-on-charcoal in ethanol, half being used for saturation of a double bond and the remainder for hydrogenolysis of halogen. The reduction product, 3-isopropyl-5-ketohexanoic acid (V), was identified by means of infrared



$$CH_3COCH_2CH\begin{matrix}\nearrow CH(CH_3)_2\\ \searrow CH_2COOH\end{matrix}$$

V

spectral comparison with a known specimen,[3] and through m.p. and m.m.p. comparisons of the oxime (94-94.5°) and semicarbazone (145-146°) of the reduction keto acid with the corresponding derivatives (95.5-96.5°; 145-147°) of authentic material.

---

[3] A.W. Crossly, J. Chem. Soc. 81, 675 (1902).

Proton magnetic resonance spectroscopy permitted final assignment of structure. Clearly discernable, in addition to signals due to two methylene and one methine hydrogens, were resonance peaks ascribable to carboxyl hydrogen; one vinyl hydrogen (unsplit); and hydrogens of the acetyl function, as well as thos of an additional isolated methyl group attached to an olefinic bond. Only the constitution assigned (IV) is consonant with the splitting pattern and chemical shifts observed in the N.M.R. spectrum of the new photoacid.

N.M.R. Data for Photoacid IV[a]

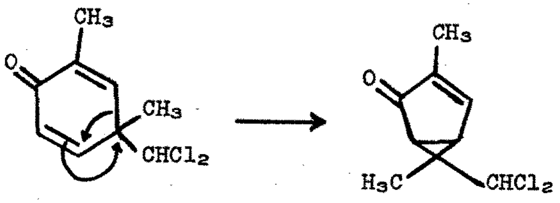
Peak (τ)	Area	Splitting	Assignment
-1.30	1	singlet	-COOH
4.01	1	singlet	$>C=CH-$
6.85	1	multiplet	$\geq CH$
7.52	4	irreg. triplet	$-CH_2-$
7.89	3	singlet	CH_3CO-
8.28	3	singlet	$CH_3C\leqslant$

[a] Spectrum was obtained on a 60 mc Varian instrument using a deuterochloroform solution at room temperature. Values relative to hexamethyldisiloxane ($\tau = 9.95$).

The exact itinerary followed by the starting dienone in the route to destination IV is obscure, although the general pathway may be surmised, at least in part. Probably the starting direction corresponds to that in the santonin ⟶ photosantonic acid case,[2,4] i.e. a bond-switching process leading to an unsaturated cyclopropyl ketone (VI). In the original example,[2] methyl migration, ring opening, double bond migration and solvation (by

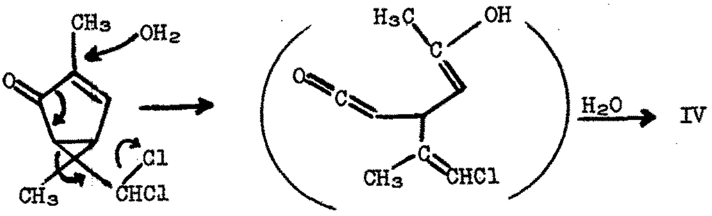
---

[4a] D.H.R. Barton, P. de Mayo and M. Shafiq, *Proc. Chem. Soc.* 205 (1957);
[b] D. Arigoni, H. Bosshard, H. Bruderer, G. Büchi, O. Jeger and L.J. Krebaum, *Helv. Chim. Acta* **40**, 1732 (1957).



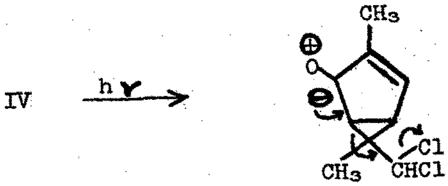
VI

processes which are still uncertain) ensue; whereas in the present case the further option of halogen elimination, in addition to ring opening and hydrolysis, is elected. In a strictly symbolic sense, presumed intermediate VI can be converted (VII ⟶ VIII ⟶ IV) to observed product without great difficulty, although it is problematical whether that process



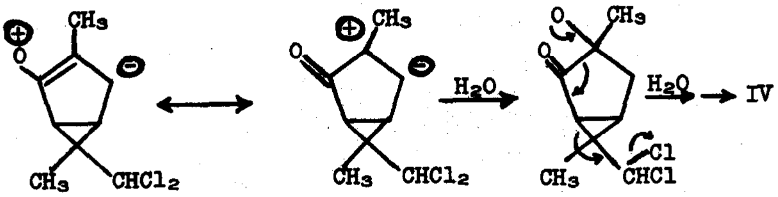
VII VIII

per se is in fact realized. Assuming that further modification of VI is photo-induced several possible initiation mechanisms present themselves, e.g. an $n \longrightarrow \pi^*$ transition leading to concerted elimination with cleavage (IX), and coupled with hydrolytic ring opening, as in VII; or, "reverse



IX

hydration" - a consequence of excited state X - followed by collapse of intermediate XI to product, as shown. It should be emphasized that the



X XI

above interpretations are illustrative only, and that further work is needed to establish the correct course of reaction.

Acknowledgment - The authors are grateful to The Petroleum Research Fund (Grant 589-C) for financial support.