

PHOTOCHEMISTRY OF DEHYDRO- β -IONONE
AND RELATED COMPOUNDS¹

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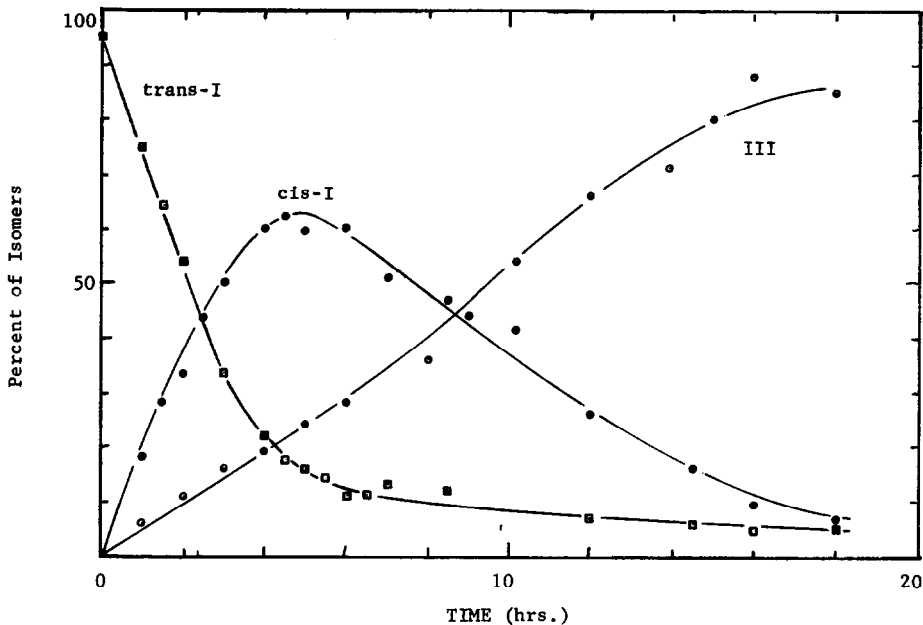
We recently reported that photosensitized irradiation of β -ionone and derivatives bypasses processes involving hydrogen migration² thus allowing only geometric isomerization.³ In fact, under selective sensitization conditions the method becomes synthetically useful for preparing 7-cis isomers in this series. For similar reasons, one might expect dehydro- β -ionone and derivatives to lead to their relatively unknown 7-cis isomers which are potential intermediates to 7-cis Vitamin A₂. Therefore, we now wish to report the photochemistry of dehydro- β -ionone (I) and its derivatives.

Direct irradiation of benzene or chloroform solution of I with light $>3,000\text{\AA}$ led to rapid disappearance of the starting material. The reaction is complete within 24 hrs. Only one final product was observed which was readily identified as the dehydrated compound II by its nmr spectrum (Table I) and by comparison of its mass spectrum with the published spectrum of II.⁴ In agreement with the structure, formation of water was clearly visible at the end of irradiation.

Upon more careful examination (nmr or glc: SE-30 column) of the solution at early stages of irradiation it becomes apparent that product II is not a primary photoproduct; but rather its formation is preceded by the simultaneous formation of two compounds. Only after significant accumulation of these compounds, formation of II becomes detectable. In fact, the latter reaction can be suppressed with the employment of proper filtering systems. Results of such

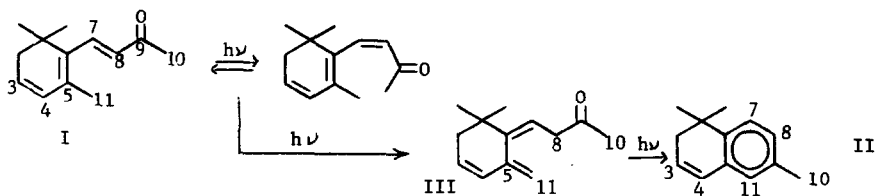
a study are shown graphically in Figure I (Corning Filter 0-54 -- approximate cut-off: 3600Å).

Figure I. Direct Irradiation (3600Å) of
Dehydro- β -Ionone^{a, b}



a. Starting material contains ~5% of II. b. In CDCl_3 .

Although so far we have not been able to isolate these two intermediates, their structure can be readily deduced from the nmr spectra of enriched samples of these compounds. The characteristic features are listed in Table I. They are products from geometric isomerization and sigmatropic rearrangement. The major primary photoproduct is cis-dehydro- β -ionone.⁵ Its formation rapidly establishes a constant trans:cis isomer ratio during the course of irradiation (Fig. I). Formation of the hydrogen migration product represents an irreversible leakage from the above "equilibrium." Finally, upon removal of the 3600Å filter, quantitative conversion of III to the dehydrated compound II was observed.



On the other hand, irradiation ($>4000\text{\AA}$) of dehydro- β -ionone in the presence of photosensitizers (fluorenone, benzanthrone, or dimethylbenzanthracene) again did not produce any amounts of the hydrogen migration product. But quite unexpectedly geometric isomerization reaction also was not observed. Prolonged irradiation of the solution only led to its darkening with eventual production of small amounts of II, the final product from direct irradiation.⁶

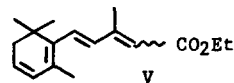
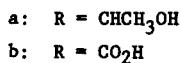
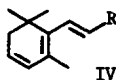
Table I
Characteristic Nmr Signals of Dehydro- β -Ionone
and Its Photoproducts^a

| | 1,1-CH ₃ | 9-CH ₃ | 5-CH ₃ | H ₇ | H ₈ | H ₃ | H ₄ |
|--|---------------------|-------------------|--|----------------------------|----------------------|--|----------------|
| | 1.06 ^d | 2.18 | 1.84 | 7.18(d) | 6.08(d) | 5.78(s) | |
| | | | | J _{7,8} = 16 Hz | | | |
| | 1.02 | 2.10 | 1.60 | 6.33(d) | 5.90(d) | 5.73(s) | |
| | | | | J _{7,8} = 12.5 Hz | | | |
| | 1.10 | 2.08 | 4.82(m) ^b 5.18(m) ^b | 5.33(t) | 3.32(d) ^c | 5.6(m) | 6.05(d) |
| | | | | J _{7,8} = 7 Hz | | J _{3,4} = 11 cps | |
| | 1.21 | 2.20 | 6.60(s) ^d | 6.82(d) | 7.05(d) | 5.78(dx)t | 6.3(d) |
| | | | | J _{7,8} = 7.5 Hz | | J _{2,3} = 4 Hz J _{3,4} = 9.0 Hz | |

a. HA-100, solvent = CDCl₃. b. exo-methylene H's. c. α -methylene H's.

d. 1 H at C-10.

The lack of chemical reaction of triplet dehydro- β -ionone appears to be general in this triene series. For example, dehydro- β -ionol (IVa) and the related acid IVb also failed to isomerize when irradiated with appropriate sensitizers.⁷ On the other hand the tetraene ester



V isomerizes when irradiated in the presence of benzpyrene to give a mixture of the corresponding 7-cis-isomers. These limited qualitative observations suggest the interesting possibility that relaxation of vertical triplets of these polyenes show high selectivity toward the lower energy half of the ring and chain portions of the conjugated chromophore. This carries some interesting mechanistic implications, and is subject to further investigations.⁸

References

1. Photochemistry of polyenes IV. For no. III in the series see ref. 3.
2. M. Mousseron, *Adv. Photochem.*, 4, 195 (1966) and references cited therein.
3. V. Ramamurthy, Y. Butt, C. Yang, P. Yang and R. Liu, submitted to *J. Amer. Chem. Soc.*
4. L. P. Stoltz, T. R. Kemp, W. O. Smith, W. T. Smith and C. E. Chaplin, *Phytochemistry*, 1970, 1157.
5. The compound does not exist in thermal equilibrium with the α -pyran isomer. Cf. *cis*- β -ionone: E. N. Marvell, G. Caple, T. A. Gosnik and G. Zimmer, *J. Amer. Chem. Soc.*, 88, 619 (1966).
6. This product is also observed in thermal rearrangement of dehydro- β -ionone. Its appearance in the sensitized reaction can be results of secondary free-radical processes.
7. Results of direct irradiation of dehydro- β -ionol and related ionylidene compounds are in the literature. See ref. 2.
8. The work is partially supported by grants from the Alfred P. Sloan Foundation and UH-Biomedical Fund.