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A PHOTOCHEMICAL SYNTHESIS OF DEHYDROCAMPHOR FROM EUCARVONE

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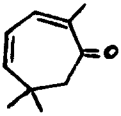
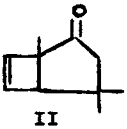
Photolysis of eucarvone (I) in 95% ethanol was reported by Büchi and Burgess[1] to give primarily the "valence tautomer" II and a small amount of III. The two isomers II and III can be equilibrated photochemically in n-hexane containing some triethylamine to a mixture of four parts II to one part. III.[1] Hurst and Whitham[2] reported that irradiation of I with sunlight in 40% aqueous acetic acid gave II and another isomer IV whose structure was assigned on the basis of infrared and chemical data. From these reports, it appears as if the course of reaction changes drastically with solvent. We have found, however, that


I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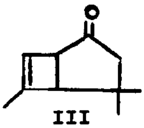
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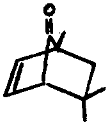
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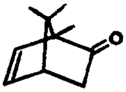
V

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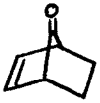
the same products are produced in these and other solvents, while the product <u>ratios</u> are solvent dependent. We have also found that another compound is formed in substantial quantities in all solvents studied, and this compound is dehydrocamphor, V. This elusive material was reported in optically active form by Asahina, <u>et</u>. <u>al</u>.,[3] and more recently by Mälkönen.[4] Its one-step synthesis from eucarvone represents an unprecedented photochemical rearrangement, and also the first synthesis of racemic V.

We have studied the photolysis of I for 7-10 days in 95% ethanol, glacial acetic acid and aqueous acetic acid (40% and 50%), utilizing a Hanovia 450-watt high-pressure mercury arc and pyrex filters in a deoxygenated system. The reactions were followed by removal of aliquots and analysis by gas-liquid chromatography. Products were isolated by distillation under reduced pressure (controls were used in all separation to insure that no products were destroyed or generated), followed by further separation by multiple refractionation on the analytical gas chromatograph. Complete separation of all products was achieved on a 10-ft. 10% w/w PDEAS-chromosorb column.

The lower boiling fractions, comprising 70-80% of the starting material, consisted of recovered I (10-25%), II (45-70%), III (5-12%), IV (1-20%) and V (10-20%). In all runs, the main product was II, whose infrared and n.m.r. spectra were essentially identical with those reported by Büchi and Burgess.[1,5] From the acetic acid runs we isolated small quantities of a compound which had the infrared spectrum reported for IV.[2] Our n.m.r. spectrum confirms the assigned structure: 3.60 τ (2 H, multiplet); 7.58 (1 H, multiplet); three singlets at 8.81, 8.90 and 9.07 τ (each 3 H) superimposed on a multiplet (2 H) at 8.5-8.8 τ. These data in conjunction with the other spectral data known for IV[2] and the parent 7-ketonorbornene VI[6] clearly establish the structure of IV. IV is apparently produced in trace amounts in 95% ethanol, and in larger quantities in the acidic solutions studied.



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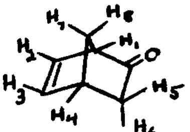
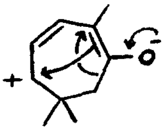


VII

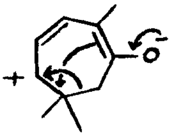
Separation of the product mixtures by gas chromatography afforded a white solid which sublimed readily and had a camphor-like odor. The mass spectrum and the elemental analysis indicated that this was yet another isomer of I. The very intense peak in the mass spectrum at m/e 108 indicates, in this series, a methylene adjacent to carbon (loss of ketene) and the peak at m/e 135 (loss of methyl) indicates a methyl probably at a bridgehead and/or allylic. The infrared band at 1740 cm^{-1} is characteristic of a carbonyl in a five-membered ring, as in compounds of type II or VII.[7] The n.m.r. spectrum in CS$_2$ shows two vinyl hydrogens at 3.63 and 4.44 τ (multiplets), multiplets at 7.37 τ (1 H) and 8.07 τ (2 H) which are in approximately the same positions, respectively, as H$_4$ and H$_{5,6}$ of VII,[7] and three sharp singlets (each 3 H) at 8.96, 9.09 and 9.14 τ for three methyl groups attached to quarternary carbon. Finally, the ultraviolet spectrum in isoöctane shows the $\pi \rightarrow \pi^*$ band at 215 mμ (ε 2610) and an enhanced $n \rightarrow \pi^*$ absorption appearing as a quartet at 287 (s) (ε 145), 298 (ε 232), 309 (ε 291) and 321 mμ (ε 215). This type of absorption has been recognized as being diagnostic of a β,γ-unsaturated ketone in a dissymmetric array, as in VII.[7,8]

On the basis of the above data, we concluded that the solid photoproduct was dehydrocamphor, V. This assignment was confirmed by direct comparison of retention times on gas chromatography and infrared spectra of our racemic compound and optically active V supplied by Mälkönen.[4,9] Mälkönen prepared optically active dehydrocamphor (V) by oxidation of dehydroborneol, and subsequently reduced his material directly to camphor.[4]

The photolysis of eucarvone (I) has thus been shown to lead to an unusually rich mixture of structurally interesting products. While it is possible to account for the formation of II and III on the basis of either radical or ionic intermediates,[1,11] the formation of IV and V by complex rearrangements seems to definitely implicate ionic intermediates.[2,10,11] The bond-breaking and bond-forming steps which, on paper, lead to IV and V are summarized in formulas VIII[12] and IX, respectively.



VIII



IX

However, on the basis of the results at this stage of the investigation, it is not clear how much mechanistic meaning to attach to such formulations since it is not as yet known whether the mechanism involves one intermediate which partitions to give the various products, or whether several competing processes are operating simultaneously. Also, there is some debate as to how many and what kinds of intermediates may precede the suggested ionic intermediates(s).[10,11] We therefore feel that any further mechanistic speculation at this time would be unwarranted. Experiments whose aim is resolving these difficulties are now in progress.

Acknowledgments

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(12) Ref. 11, p. 355.