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PHOTOISOMERIZATIONS, VII[1]. A BICYCLO[3.1.0]HEXENE FROM ALLOOCIMENE.

K. J. Crowley

Department of Chemistry, Instituto Venezolano de
Investigaciones Científicas, Apartado 1827, Caracas,
Venezuela.

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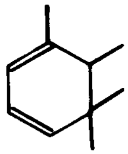
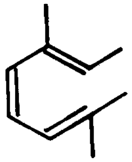
Ultraviolet irradiation of alloocimene (II) is known to give α-pyronene (I)[2] and a 1,2,4-triene (III).[3] The concomitant formation of another photoisomer (IV) is now reported.[4] This product,* b.p. 61°/37 mm., was isolated by distillation in 14% yield, after irradiation (λ> 250 mμ) of a 5% hexane solution of II at 50° until the UV absorption at 270 mμ was reduced to 8% of the original value.

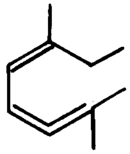
Its UV (λ_{max} 212 mμ, ε 5000) and IR spectra are consistent with the structure (IV). Its NMR spectrum† shows the vinyl methyl at 1.67 δ (diffuse s), the secondary at 1.05 δ (d, J = 7 c/s), and the other two at 1.04 and 0.82 δ (both s); the



I



II



III

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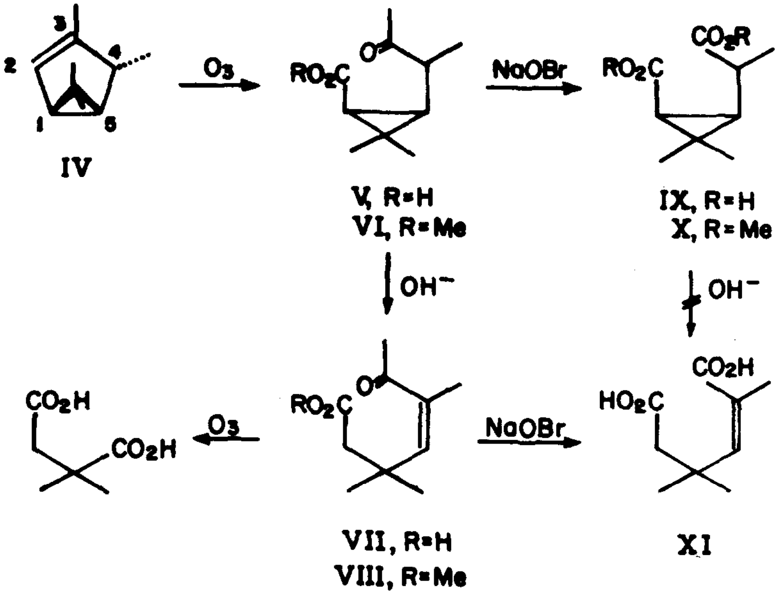
* Satisfactory carbon and hydrogen analysis obtained.

† All NMR data were obtained on a Varian A-60 and double irr iations were done with a V-6058 spin decoupler accessory; every case the integrated proton ratios were in agreement the assignments made: s = singlet; d = doublet; m = multi

vinyl proton absorbs at 5.26 δ (diffuse s). Double irradiation experiments permitted the location of H_1 at 1.6 δ (d, J ~ 6 c/s), of H_5 at 0.98 δ (d, J ~ 6 c/s) and of H_4 at 2.06 δ (approx. quartet, J ~ 7 c/s). The illustrated configuration of the secondary methyl group follows from the fact that $J_{4,5}$ ~ 1 c/s so that the two protons are roughly at right angles.

On treatment with ozone and then with hydrogen peroxide in methanol, the photoproduct gave the keto-acid* (V), m.p. 91-2° (38%). This had appropriate UV, IR and NMR spectra, and was oxidized with sodium hypobromite to the dicarboxylic acid* (IX), m.p. 160-2°, in 78% yield. The latter yielded a glutaric (ν_{max} 5.57 and 5.71 μ) anhydride,* m.p. 34-41°, which gave the parent acid on hydrolysis.

Treatment of the corresponding keto-ester (VI) for 3 hr. with refluxing 10% methanolic potassium hydroxide, and reësterification of the product,gave starting material (25%) and the unsaturated keto-ester (VIII)(73%). The free acid (V) undergoes ring opening more slowly, and with the formation of more by-products. The ester (VIII), λ_{max} 292 mμ (ε, 83), λ_{max} 223 mμ (ε, 13900)(in ethanol), showed appropriate IR maxima, and, on ozonolysis followed by performic acid oxidation, gave 2,2-dimethylsuccinic acid (identified by mixed m.p. and IR spectrum). The unsaturated keto-acid (VII) was not obtained in crystalline form, but, on oxidation with sodium hypobromite, gave the dicarboxylic acid* (XI)(32%), m.p. 122-122.5°, λ_{max} 212 mμ (ε .2000).

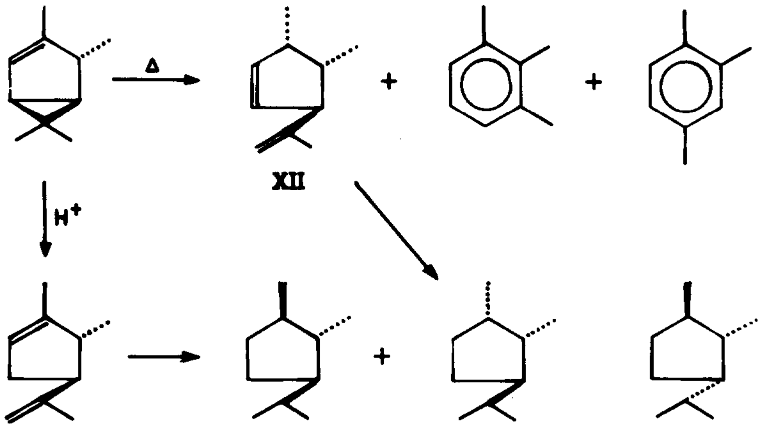


Attempted ring opening of the di-ester (X) under the same conditions gave only starting material and two minor products (2% and 1%), neither of which was the aliphatic acid (XI). This indicates a marked destabilization of the intermediate anion by the α-methyl group, since the corresponding compound without this methyl, cis-homocaronic acid, undergoes ring opening to the extent of 39% under these conditions.[5]

On pyrolysis at 330° for 60 min., the photoproduct yields 59% of volatile material, mainly the cyclopentene (XII) (54%), 1,2,3-trimethylbenzene (8%) and 1,2,4-trimethylbenzene (8%). These were isolated by gas chromatography, and the aromatic compounds identified by their IR and NMR spectra. The cyclopentene* (XII) gives IR maxima corresponding to the $>C=CH_2$ (3.25, 5.6, 6.09 and 11.27 μ) and <u>cis</u> -CH=CH- (3.30, 6.04 (sh) and 13.9 μ) groups, and shows λ_{2000} 211 mμ. In its NMR spectrum, the isopropenyl group gives maxima at 4.73 (m) and 1.67 δ (m), decoupled on double irradiation, while the other features include the vinyl protons at 5.64 δ (m), and secondary methyl groups at 0.95 (d, J = 7.1 c/s) and 0.88 δ (d, J = 7.2 c/s); decoupling experiments showed the corresponding tertiary protons to be centred at 2.1 and 2.8 δ respectively.

On hydrogenation of XII, one main product* (XIV) was obtained (73%). The illustrated stereochemistry of these two compounds follows from that of IV, since the thermal isomerization evidently proceeds by a 1,5-homodienyl hydrogen shift,[6] which requires that the 3-methyl and 5-isopropenyl groups of XII be <u>trans</u>.

On acid-washed alumina the photoproduct isomerizes exothermically to another cyclopentene* (XIII), b.p. 87°/82 mm (45%). This has λ_{1000} 214 mμ, ν_{max} 3.29, 6.04 (sh), and 12.48 μ (>C=CH-), and 3.25, 5.61, 6.09 and 11.25 μ ($>C=CH_2$), while its NMR spectrum shows the secondary methyl group at 1.04 δ (d, J = 6.5 c/s) and gives singlets with fine splitting at 5.43 (=CH-), 4.86 ($C=CH_2$), 2.4 (allylic $-CH_2$), and 1.74 δ (two vinyl methyl groups). It yielded two main tetrahydro-derivatives; the minor (15%) gave the IR spectrum of (XIV). The major product* (XV)(78%) shows IR maxima similar to, but definitely different from, those reported[7] for this compound. It appears that the previously reported compound was XVI, and that its isopropenyl parent was converted to



XIII XV XIV XVI

1-*trans*-2-*cis*-3-trimethylcyclopentane by procedures[7] in which intermediates suffered epimerization[8] to the more stable *trans* configuration; the later mechanism suggested[9] for the formation of the parent compound implies that the isopropenyl and adjacent methyl groups are *cis*.

Irradiation of α-pyronene (I) also gives mainly IV. The rates of formation of the latter during the early stages of the irradiations of *allo*ocimene and α-pyronene suggest that it is formed directly from one of the 4-*cis*-*allo*ocimenes. It was not possible by this method to determine whether IV is also formed directly from α-pyronene.

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