

PHOTOISOMERIZATION OF CONJUGATED CYCLOPROPYL KETONES¹

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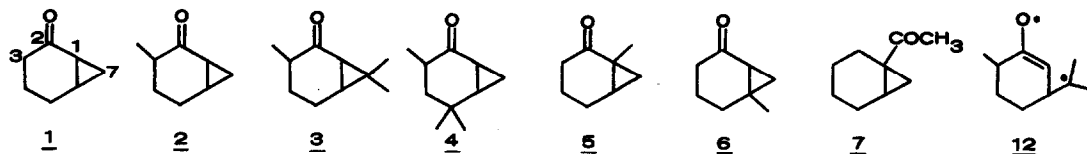
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(Received in U.S.A. 14 July 1967)

The cis-trans photoisomerization of conjugated cyclopropyl ketones is well established³ and their isomerization to α,β -enones has frequently been reported.⁴ In bicyclo[n.1.0]alkane-2-ones the two cyclopropyl bonds unsymmetrically overlap with the carbonyl π -lobes. This is experimentally indicated by their u.v. spectra,⁵ and should perhaps lead to specific or selective photo-cleavage of the better-overlapped bond. This specificity has already been observed in the lithium/ammonia opening of cyclopropyl ketones⁶ and several photoisomerizations of rigid cyclopropyl ketones to α,β -enones⁴ suggest that rearrangement occurs only by breakage of that cyclopropyl bond with optimum geometry for overlap with the carbonyl group.

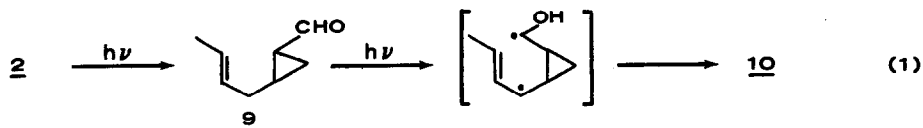
This study involves bicyclic[4.1.0]ketones 1-7, where the C₁-C₇ bond is the geometrically preferred position for photolytic cyclopropyl cleavage in ketones 1-6. The C₇-unsubstituted ketones were obtained by allowing dimethyl-oxosulfonium methylide to react with the corresponding enones,⁷ and 2-carone (3) was synthesized by the addition of hydrogen chloride to dihydrocarvone, followed by intramolecular enolate displacement of the chloride.⁸

The irradiation⁹ of 1 yielded 3-methyl-2-cyclohexenone (8) as the major volatile photoproduct (16%), which was identical to an authentic sample. The low yield is probably due to dimerization of 8.¹⁰ There was also 1-2% of another unidentified product.



The irradiation of 2 proceeds differently from 1 in that the major product (44%) is an aldehyde, identified as $\Delta^{4,6}$ -octadienal (10) on the basis of the following data: mol. wt. 124 (mass spectrum); ν_{\max} 2817, 2710, 1730 cm^{-1} ; $\lambda_{\max}^{95\% \text{ EtOH}}$ 228 $\text{m}\mu$ (ϵ 20,400); nmr (τ , ppm), 0.53 (1 H, broad singlet, aldehydic H), 3.57-4.83 (4 H, multiplet, vinylic H), 7.53 and 7.58 (4 H, two broadened singlets, methylene H), 8.28 (3 H, doublet, $J = 6$ cps, vinylic methyl). The doublet multiplicity of the vinylic methyl group, and the resonance position of the methylene hydrogens,¹¹ eliminate the $\Delta^{3,5}$ -isomer as a possible structure. Lithium aluminum hydride reduction of 10, followed by hydrogenation, yielded n-octanol. In addition to 10, there was found a second aldehyde (14%), which was identified as 2,3-methano- Δ^5 -heptenal (9): mol. wt. 124 (mass spectrum); ν_{\max} 2817, 2706, 1708 cm^{-1} ; $\epsilon_{220 \text{ m}\mu}$ 2,310, $\epsilon_{187.5 \text{ m}\mu}$ 13,000; nmr (τ , ppm), 0.77 (1 H, doublet, $J = 4$ cps, aldehydic H), 4.42-4.74 (2 H, multiplet, vinylic H), 7.43-8.52 (7 H, multiplet with a doublet of doublets at 8.35, $J = 3.5$ cps, $J' = 1.5$ cps), 8.68 and 8.93 (2 H, two misshapen doublets, $J = 8.5-9.0$ cps, cyclopropyl H). Isolation and reirradiation of 9 rapidly produces 10 in good yield.

The formation of 10 is viewed as arising from the well-known Type I reaction¹² of cyclic ketones to yield unsaturated aldehydes, followed by a Type II reaction¹² involving 9 (eq 1). The proposed second step of eq 1 is similar to the finding that 1,1-dimethyl-2-acetylcyclopropane photochemically yields



5-methyl- Δ^5 -hexene-2-one.¹³ Merely the addition of a 3-methyl group to the 2-norcarone skeleton has excluded any product developing from a cyclopropyl ring cleavage as the primary photochemical step.

Irradiation of 3 yields products derived from both cyclopropyl ring opening and from α -cleavage. Rupture of the $\text{C}_1\text{-C}_7$ bond leads to 3-isopropyl-6-methyl-2-

cyclohexenone (26%), identical to a synthetic sample,¹⁴ and α -cleavage yields 3,3-dimethyl- $\Delta^{4,6}$ -octadienal (11) (19%). Aldehydic 11 has spectral characteristics analogous to those of 10 except that a cis-trans mixture about the C₄-C₅ double bond is assigned on the basis of the nmr spectrum. The aldehydic proton appears as two overlying triplets at τ 0.60 and 0.64 (1 H, J = 3 cps) and the gem-dimethyl group as three singlets at τ 8.73, 8.82, and 8.86 (6 H, the former two singlets are equal in intensity and the latter singlet is twice as intense). The C₄-C₅ trans isomer should show magnetically equivalent methyl groups (8.86) whereas the cis isomer should not, due to severe rotational hindrance about the C₃-C₄ single bond. Aldehyde 10 is also probably a cis-trans mixture. Reduction of 11 yielded 3,3-dimethyloctanol, which was identical to a synthetic sample.¹⁵

A glc peak (6%), corresponding to a compound analogous to aldehyde 9, was seen during the irradiation; however, this product was unable to be isolated. Two other minor photoproducts (4%) also were not identified.

From the photochemical behavior of 2, ketone 3 would be expected to yield a diene aldehyde product. The reason for the additional appearance of an enonic product probably is because C₇-disubstitution stabilizes the radical-like intermediate 12 enough to allow cyclopropyl ring opening to compete efficiently with α -cleavage. Ketone 2, without this stabilization, yields only α -cleavage products. This same reasoning can explain the behavior of 1, where unsubstitution at C₃ prevents α -cleavage from competing with the cyclopropyl ring opening.

Ketone 4 was designed to prevent the second step of eq 1. Irradiation of 4 yielded 2,3-methano-4,4-dimethyl- Δ^5 -heptenal (13) (38%): mol. wt. 152 (mass spectrum); ν_{\max} 2857, 2710, 1709 cm⁻¹; $\epsilon_{220 \text{ m}\mu}$ 1,830, $\epsilon_{195 \text{ m}\mu}$ 9,610; nmr (τ , ppm), 1.18 (1 H, doublet, J = 6 cps, aldehydic H), 4.52-4.75 (2 H, multiplet, vinylic H), 8.14-8.42 (4 H, multiplet with a doublet of doublets at 8.33, J = 3 cps, J' = 2 cps, vinylic methyl and proton α to the carbonyl), 8.43-9.04 (6 H, multiplet with a very strong singlet at 8.88, gem-dimethyl). The alcohol obtained from reduction of 13 provided additional evidence for the cyclopropyl ring because the nmr spectrum shows complex absorption from τ 8.60-9.94. This high field absorption is very characteristic of cyclopropyl hydrogens.¹⁶

Irradiation of 5 yielded 25% of 2,3-dimethyl-2-cyclohexenone and 8% of several minor unidentified products. Increased substitution at C₁ does not facilitate α -cleavage between the carbonyl group and the cyclopropyl ring, probably due to increased bond order of the C₁-C₂ bond in the excited state (see 12).

Ketone 6 has no proton at C₆, which by an intramolecular migration could yield enonic photoproducts similar to those found from ketones 1, 3, and 5. Irradiation of 6 results in only a very slow disappearance of starting material with only trace amounts of volatile photoproducts being formed. Even though opening of the C₁-C₆ bond would give a very stable tertiary radical at C₆, the unfavorable geometry for conjugation of the carbonyl group with this arm of the cyclopropyl ring apparently prevents this mode of reaction.

Ketone 7, with equal conjugative overlap of both cyclopropyl bonds, has recently been reported¹⁷ to photoisomerize to 1-acetylcycloheptene. Similar results were found in this study. A second volatile photoproduct (2%) formed from the irradiation of 7 has been tentatively identified as 1-acetyl- Δ^2 -cycloheptene (14): ν_{\max} 1715 cm⁻¹; nmr (τ , ppm), 4.10-4.32 (broad peak, vinylic H), 6.66-7.04 (weak, broad peak, proton flanked by carbonyl group and double bond). This spectral data eliminates 1-acetyl-2-methylcyclohexene, expected from opening of the C₁-C₇ cyclopropyl bond, as a structure for 14.

These results allow the following generalizations to be made regarding the photoisomerizations of bicyclo[4.1.0]heptane-2-ones: (1) Cyclopropyl ring opening as a primary process can compete with α -cleavage of the C₂-C₃ bond only when C₃ is unsubstituted or when C₇ is substituted; (2) When cyclopropyl ring opening occurs as a primary process, only that bond which conjugates best with the carbonyl group will open.¹⁸ Also, when both cyclopropyl bonds can overlap equally with the carbonyl group, only that bond with the highest degree of terminal substitution will open, and, in cyclopropyl conjugated carbonyl compounds, like 9, Type II reactions will predominate if γ -hydrogens are present, provided the geometry of the system is such that these can be abstracted by the carbonyl oxygen.

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