Thermal Isomerization of β-Ionylideneacetaldehyde. Isolation of a Tricyclo[5,4,0,$0^{1,5}$]undec-3-en-6-one

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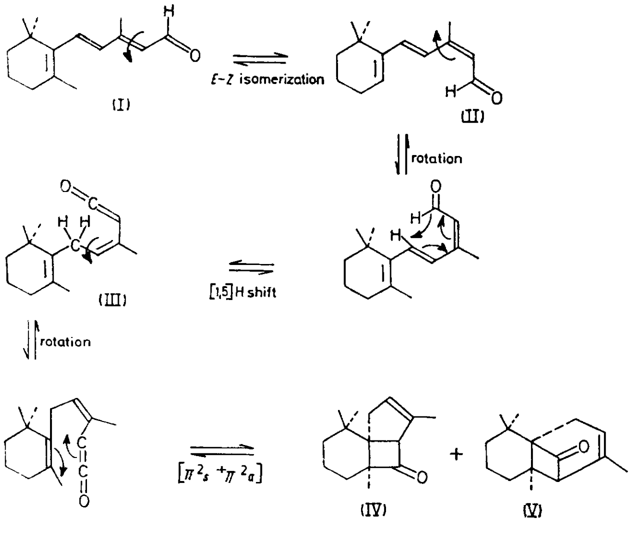
Summary β-Ionylideneacetaldehyde (I) can easily be isomerized thermally to a tricyclic ketone (IV), probably *via* an initial *E*-to-*Z* isomerization of the double bond adjacent to the carbonyl group, followed by a [1,5]sigmatropic hydrogen shift; the resulting keten (III) interacts with the double bond of the cyclohexene ring to give the [2 + 2] cycloadduct (IV).

β-IONYLIDENEACETALDEHYDE is an important intermediate in several syntheses of vitamin A.[1] It can be obtained conveniently from β-ionone by various routes. Its purification and characterization are not without problems because of its thermal instability.[2] The failure reported by Heilbron,[3a] Krauze,[3b] and Karrer[3c] to reproduce the first synthesis of vitamin A of Kuhn and Morris,[4] which also proceeded *via* β-ionylideneacetaldehyde, may be attributed to isomerization of this aldehyde.



Unless special conditions are used, distillation *in vacuo* of crude β-ionylideneacetaldehyde will yield a product which shows a much lower u.v. absorption than the starting material. From the distillate a crystalline compound ($C_{15}H_{22}O$, m.p. 63—64°; semicarbazone m.p. 227—229°) can be isolated in a yield of *ca.* 50%. This compound is essentially transparent in the u.v., except for a weak absorption at 315 nm (ϵ = 180 in MeOH).[5] Structure (IV) is in accord with spectral data (i.r., n.m.r., and m.s.) and has been confirmed by *X*-ray analysis.[6] A reasonable route for the formation of this ketone is indicated in the Scheme.

The first step, a reversible *E*-to-*Z* isomerization of the double bond adjacent to the carbonyl group, due to thermal excitation, may be rate-determining since the reaction proved to be accelerated by general acid catalysis. The rates of the following steps are considered to be independent of added acid.

A thermally allowed suprafacial [1,5] sigmatropic shift of the aldehydic hydrogen is involved in the second step of the reaction, leading to the intermediate keten (III). Proof of this rearrangement was obtained from a labelling experiment in which the aldehydic hydrogen was substituted for deuterium. Under the reaction conditions the intermediacy of a keten could not be established directly by i.r. spectroscopy (no absorption in the 2150 cm^{-1} region). The keten may be a transient species with a short lifetime, as is known to be the case in several related reactions.[7]

Models indicate that the required orthogonal geometry of the reacting double bonds for the subsequent thermally induced [2 + 2] cycloaddition can be easily realized despite the presence of several neighbouring methyl groups. Thus it is plausible that the proposed third step of the sequence can proceed rapidly. The $[_{\pi}2_s + _{\pi}2_a]$ condition for the reaction to be thermally allowed can be fulfilled in two ways and therefore two geometric isomers, (IV) and (V), are to be expected.[8] The simultaneous formation of two reaction products was in fact observed by g.l.c. As the reaction proceeded, one of these products was found to be isomerized to the other, suggesting a thermal equilibrium. The composition of the reaction mixture will thus be determined by thermodynamic control. Obviously this is in favour of compound (IV), since this product proved to be the main component of the reaction mixture.

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