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SYNTHESIS AND PHOTOCHEMISTRY OF 2,3,8,9-TETRAHYDROINDENONE-1[1]

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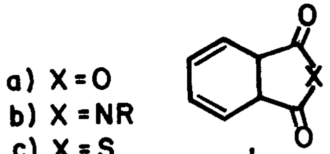
Abstract. The novel β,γ,δ,ε-unsaturated ketone (2) was prepared and all its photoproducts were identified, following wavelength dependent, irradiation-induced transformations.

We are engaged in a research project on β,γ,δ,ε-unsaturated carbonyls, in the framework of which we have dealt up to now with the symmetric 1,2-dihydrophthalic derivatives namely the anhydride (1a)[3], the imides (1b)[1] and the thioanhydride (1c)[4].

The next and most interesting subject of study was the corresponding keto-system with various geometries[2a] and we present now the results of a study on the irradiation-induced transformations of the first member in a series of cyclohexa-2,4-dienyl ketones, namely 2,3,8,9 tetrahydroindenone-1 (2). After a number of attempts, 2 was eventually prepared in a sequence of reactions starting with the dimer (3) of cyclopentadienone diethylketal[5], which undergoes facile acid-catalysed partial hydrolysis to the diketone-mono-ketal (4)[6]. The latter underwent 1,4-reduction by $LiAlH_4$ at -70°C, affording 5, which was converted to the diketone (6) by BF_3-etherate/acetone transketalisation. Eventually, pyrolysis of 6 in very special conditions, viz. in the gas phase, at 10^{-4} torr and 350°, by subliming it into a suitable heated coil attached to a vacuum system via a liquid nitrogen trap, provided pure 2 (98%), as a colorless oil, ν_{max} 1735 cm^{-1}, λ_{max} (MeCN) 263 (3500), 268 (3300) nm.



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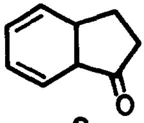

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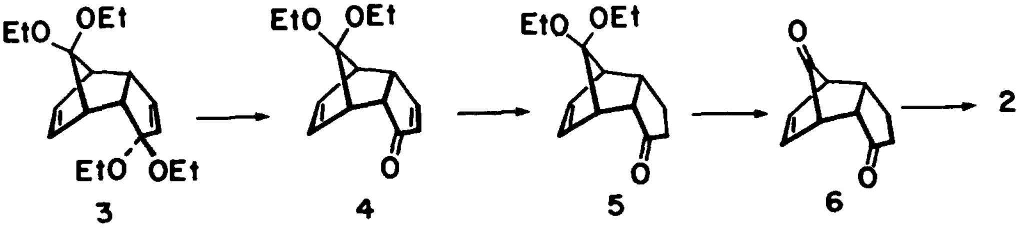
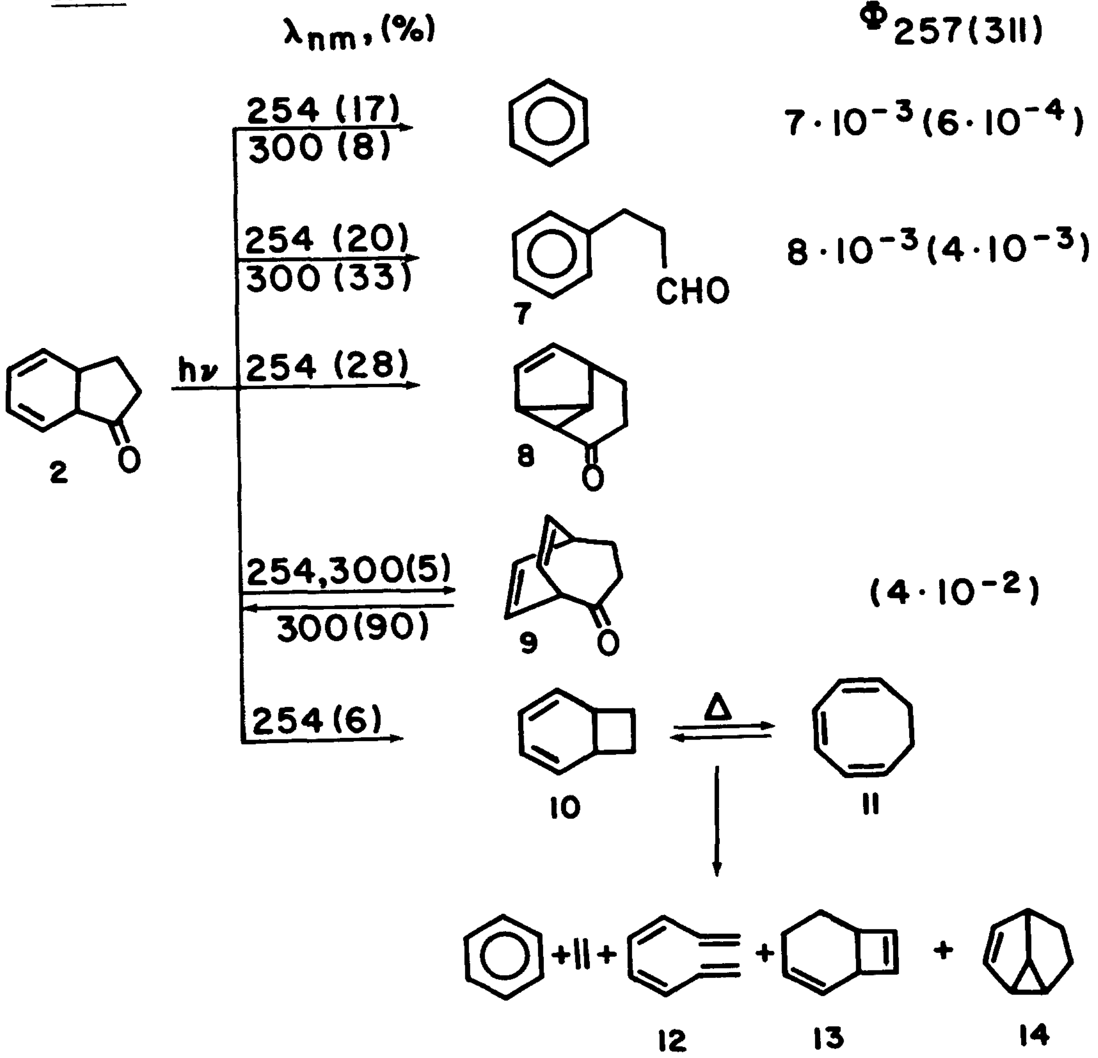


Direct irradiation of 2 in MeCN, gave, in wave-length dependent chemical and quantum yields (see Scheme): benzene, 3-phenylpropanal (7), the 1,2-acyl-shift-product (8), the 1,3-acyl-shift-product (9), and the decarbonylation products 10-14 along with ethylene next to benzene[7-11]. Furthermore, up to 5% dimeric products were isolated.

Actually, of the isomeric hydrocarbons 10-14, octatetraene (of unspecified configuration) (12) was the first to be detected by its strong long-wavelength UV absorption[12], in the 254 nm irradiation product-mixture, and isolated as its bromination product. Next, a more concentrated solution of 2 was irradiated and monitored by glpc, whereby all the mentioned hydrocarbons (ca. 6%) were identified and compared to the products which were obtained in independent photolyses of authentic 10 and 11[13], following previous reports[7-9] but retaining our conditions. These processes are relatively well understood from both flash-[10] as well as stationary solution-[7-9] and matrix[11] photolyses. It should also be stated that we saw none of those products at 300 nm and above.

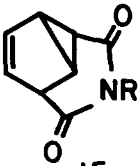
SCHEME



The 1,2-rearrangement product 8 was correctly identified only after extensive double-irradiation NMR measurements along with deuterium labeling techniques. The striking feature in its formation is the fact that it is an *ordinary* oxa-di-π-methane photo-rearrangement product, i.e. involving the carbonyl and *one*, β,γ-positioned double bond.[16] This is in contrast to the behaviour of the related 1,2-dihydrophthalimides (1b)[1], where a 1,2-rearrangement to 15 occurred, involving *both* double bonds in the electron redistribution process. We seek the explanation to this apparent discrepancy, in a different orbital level ordering in 2 as compared to 1b.

The 1,3-rearrangement product (9), was sought following an observation by Kende on the photo-rearrangement of 16 to 17.[14] While routine examination of the irradiation mixture was fruitless, we were able to detect (9) therein (glpc, nmr) (up to *ca.* 5% and decreasing with time) only after having compared it with an authentic sample (9) which we had independently prepared by Zn$^-$/AcOH reduction of 18[15]. It turns out, in fact that the reverse photoreaction (9 → 2) is the more efficient one (ϕ_{311} = 0.04, 90% yield).

We tend to invoke the intermediacy of a diradical species (19) as a result of efficient α-cleavage of 2, leading to the total fragmentation product benzene, along with the decarbonylation products 10, 11 and the hydrogen-transfer-product 7. It seems that 19 is not involved in the formation of 8 and 9, but it is hard to say anything conclusive at this stage. This and other mechanistic problems, are being looked into by radical trapping and photophysical work, now in course.



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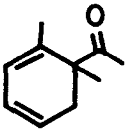

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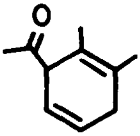

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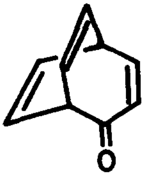

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References and Notes

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