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PHOTOCHEMICAL CYCLIZATION OF 5-HEXENAL

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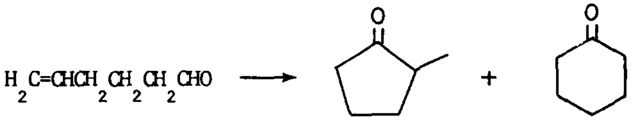
The photochemical addition of aldehydes to olefins yielding saturated ketones was first described some twenty years ago.[3] Although the reaction seems to have received little attention, studies and examples have been recorded sporadically.[4] We wish to report the occurrence of this transformation upon irradiation of 5-hexenal (1) and to point out its relevance to the photochemistry of cyclohexanone.

Irradiation of a dilute (20 mg/ml) acetone solution of 5-hexenal[5] with a 450 watt medium-pressure mercury arc (Hanovia type L, no. 679A-36) for twelve hours through Pyrex led to destruction (>95%) of the starting aldehyde and formation of a variety of products as judged by vapor phase chromatography (vpc).[6] Two of these, tentatively identified by retention times as 2-methylcyclopentanone (2) and cyclohexanone (3), were isolated by preparative vpc. The identification was fully confirmed by comparison of ir and nmr spectra, as well as comparison of melting point, mixture melting point, and ir spectra of the known[7] derived 2,4-dinitrophenylhydrazones, with those of the appropriate authentic substances. From calibrated vpc integrals the yield of 2-methylcyclopentanone was found to be 4% and that of cyclohexanone, 2%. Similar irradiation of 5-hexenal in n-pentane failed to yield detectable amounts of either ketone.



$H_2C{=}CHCH_2CH_2CH_2CHO$

1 2 3

The lower homolog, 4-pentenal, undergoes gas phase photolysis sensitized by benzene triplets,[8] and there is inferential evidence[8] that this process involves an olefin triplet which intramolecularly attacks the aldehydic hydrogen of ground state carbonyl. It is plausible that a similar pathway is followed by 5-hexenal in solution, and such a mechanism provides a reasonable explanation for our observation of the reaction in acetone but not in pentane. In acetone the olefin triplet is accessible via transfer of energy from acetone triplets.[9] In pentane, however, all light is initially absorbed by the aldehyde carbonyl; intersystem crossing to the carbonyl triplet and subsequent transfer to form olefin triplets must in this case compete with the several alternative reactions available to the carbonyl excited singlet and triplet species.

This cyclization of 5-hexenal provides an attractive explanation for the curious formation of small amounts of 2-methylcyclopentanone upon irradiation of cyclohexanone, either neat or in cyclohexane solution.[10] The main monomeric product of this reaction is 5-hexenal[10, 11, 12] and it seems clear that 2-methylcyclopentanone can be formed by secondary photochemical transformation of the aldehyde, with unreacted cyclohexanone serving as triplet sensitizer. Previously 2-methylcyclopentanone has been regarded[10] as a primary photoproduct arising directly from cyclohexanone *in a novel rearrangement involving hydrogen migration and concomitant ring contraction.*

We have prepared 5-hexenal from commercially available 5-hexen-1-ol. The derived tosylate, prepared from the alcohol in the usual fashion, was oxidized without prior rigorous purification by exposure to dimethyl sulfoxide and sodium bicarbonate at 150° for six minutes.[13] The aldehyde, formed in 46% yield and purified by distillation and preparative vpc, was characterized by preparation of the 2,4-dinitrophenylhydrazone[14] and by ir and nmr spectroscopy.

FOOTNOTES AND REFERENCES

(1) Fellow of the Alfred P. Sloan Foundation.

(2) National Science Foundation Graduate Fellow.

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(4) For example, H. H. Schlubach, V. Franzen, and E. Dahl, Ann., **587**, 124 (1954); and P. de Mayo, J. B. Stothers, and W. Templeton, Can. J. Chem., **39**, 488 (1961).

(5) Preparation of this compound is described below.

(6) All vpc was carried out on a Varian Aerograph 700 Autoprep operated at 100° with a helium flow rate of 100 ml/min and using a 20 ft x 0.25 in. stainless steel column packed with 30% SE-30 on 60/80 Chromosorb W.

(7) 2-Methylcyclopentanone 2,4-dinitrophenylhydrazone: A. S. Dreiding and J. A. Hartman, J. Am. Chem. Soc., **75**, 943 (1953); cyclohexanone 2,4-dinitrophenylhydrazone: C. F. H. Allen, ibid., **52**, 2958 (1930).

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(9) R. E. Rebbert and P. Ausloos, J. Am. Chem. Soc., **87**, 5569 (1965).

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(13) N. Kornblum, W. J. Jones, and G. J. Anderson, J. Am. Chem. Soc., **81**, 4113 (1959).

(14) This derivative gave satisfactory analysis for carbon, hydrogen, and nitrogen and melted at 104°. It has been previously reported (ref. 12) with m.p. 93-94°.