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INTRAMOLECULAR ENE-SYNTHESIS OF PHOTOACTIVATED CARBONYL COMPOUNDS[1]

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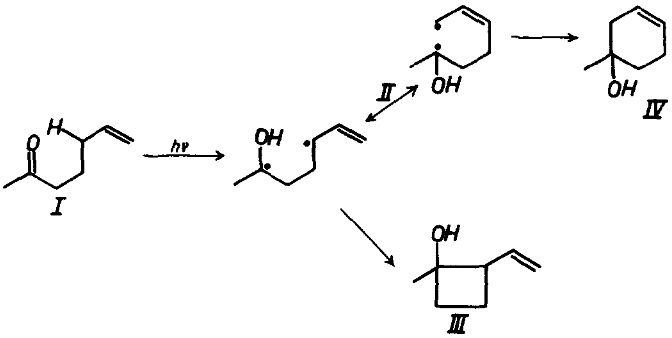
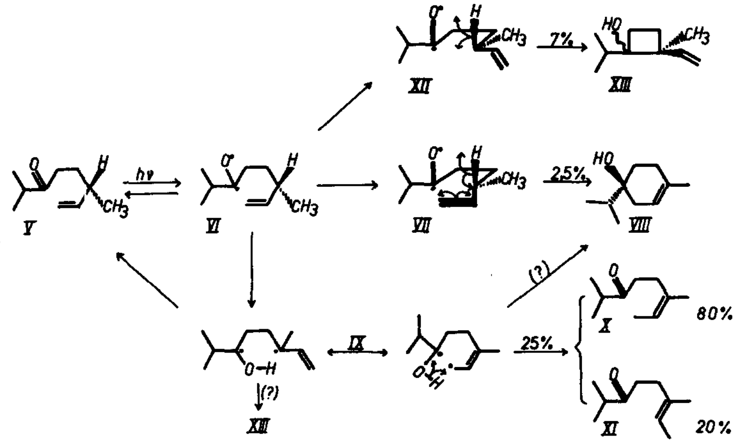
Photochemically excited aliphatic ketones with a γ-hydrogen atom form cyclobutanols[2]. If, in addition, the γ-hydrogen is in the allyl position as in I, cyclohexen-ol (IV) is obtained as well as III[3]. This led to the mechanistic conception of the formation of III and IV through an initially formed allyl mesomeric diradical (II)[3].



Such a stepwise formation of IV did not seem to us unambiguously proved, since the conversion I ⟶ IV exhibits characteristic indications of an intramolecular ene-synthesis[4] involving a many-centered process[5].

Using the photolysis of (6S)-(+)-2,6-dimethyloct-7-en-3-one (V)[6] as an example we have been able to confirm our supposition, in that we found (4S)-(+)-terpinen-4-ol (VIII) ($[\alpha]_D^{20}$ +27.1°)[8] among the irradiation products[7] of V. The formation of VIII with retention of configuration[9] is, therefore, not possible by way of an allyl radical (IX) corresponding to II, but must be associated with a one-step reaction mechanism.



Furthermore, the intermediate appearance of the free allyl radical (IX), arising by intramolecular dehydrogenation of the photochemically excited ketone (VI) is derived from the formation of the isomeric ketones (X) and (XI), and the racemisation[9] of the starting material (V) during the irradiation[10]. This racemisation is explicable by a "head-to-tail" disproportionation[11] of the 1,4-diradical (IX).

Depending on the participation of the vinyl group in the photochemical reaction, a *intramolecular six-centre reaction of the indirect substitution type involving addition in the allyl position* (VII)4) leads to the formation of optically active terpinen-4-ol (VIII). On the other hand cyclobutanol formation occurs by *stereospecific removal of the allyl γ-H-atom in a four-centre process* XII12), and is similarly one-step. The fact that only one of the possible stereoisomers of XIII is formed implies a definite stereochemistry of the substituents at the reaction centres.

The formation of VIII or XIII by combination of the resonance-stabilized allyl radicals IX will play only a relatively unimportant part13) - if indeed it occurs at all, since the loss of optical activity in the cyclisation products (VIII)9) and (XIII)14) can hardly be a consequence of the cyclisation, but rather of partial racemisation of the ketone (V). With only brief irradiation, racemisation of the starting ketone (V) falls, the optical purity of the cyclisation products rising to the corresponding extent.

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3) N.C. Yang, A. Morduchowitz and D.H. Yang, *J. Amer. Chem. Soc.* **85**, 3033 (1963)

4) K. Alder, H. Söll and H. Söll, *Liebigs Ann. Chem.* **565**, 75 (1949)

5) Several examples of the thermally induced intramolecular "Ene-Synthesis" of similar carbonyl compounds have been published: G. Ohloff, *Tetrahedron Letters* **1960**, No 11, 10; G. Ohloff, *Angew. Chem.* **72**, 569 (1960)

6) V ($[\alpha]_D^{20}$ +9.8°) was prepared from (6S)-(+)-2,6-dimethylocta-2,7-diene ($[\alpha]_D$ +9.5°) via (6S)-(+)-2,3-epoxy-2,6-dimethyloct-7-ene ($[\alpha]_D$ +11.1°).

7) Ketone V was irradiated as a 10% solution in cyclohexane with a high pressure mercury lamp (Philips HPK 125 W) in a quartz vessel until 95% conversion of starting material had occured.

8) The (4R)-configuration has been assigned to (-)-terpinen-4-ol chemical means; this will be reported in detail elsewhere.

9) The rotation of the starting ketone ($[\alpha]_D^{20}$ +9.8°) corresponds to a value of $[\alpha]_D^{20}$ +43.8° for terpinen-4-ol. Based on this, and on 95% conversion of V, the (+)-terpinen-4-ol isolated, with its rotation of $[\alpha]_4^{20}$ +27.1°, corresponds to 62% optical purity. The recovered starting material (V) (5%) from the same photolysis consisted of 76.5% racemate ($[\alpha]_D$ +2.4°).

The possibility of racemisation by intramolecular dehydrogenation of V via VI and IX to V cannot be excluded in the light of our present work. P. de Mayo, J.B. Stothers and W. Templeton, Can. J. Chem. **39**, 488 (1961) have reported the intramolecular racemisation of (+)-carvomenthone by photochemically excited acetone.

10) The proportion of 2-methylbutan-3-one and isoprene among the photolysis products of V comes to a total of 55%. Concerning this photo-fragmentation cf. R.G.W. Norrish, Trans. Faraday Soc. **33**, 1521 (1937)

11) K.J. Ivin and E.W.R. Steacie, Proc. Roy. Soc. [London], A **208**, 25 (1951); cf. Lapporte, Angew. Chem. **72**, 759 (1960)

12) J. Orban, K. Schaffner and O. Jeger, J. Amer. Chem. Soc. **85**, 3033 (1963) have observed a photochemical cyclobutanol formation from corresponding saturated aliphatic carbonyl compounds with partial retention (max. 24%) of configuration. We have found, in the case of (-)-2,6-dimethyloctan-3-one ($[\alpha]_D^{20}$ -9.4°) as well as with V, a significant racemisation which depends on the irradiation duration. At 50% conversion of the starting material, its rotation had already fallen to $[\alpha]_D^{20}$ -6.05°. In view of this fact, the retention value quoted by Orban, Schaffner and Jeger requires a corresponding correction.

13) Kinetic measurements will show to what extent free radicals must be eliminated from consideration in the cyclisation.