

Base-catalyzed and Photolytic Rearrangements of 4,5,6-Triphenyltricyclo[2,1,1,0^{5,6}]hexan-2-one

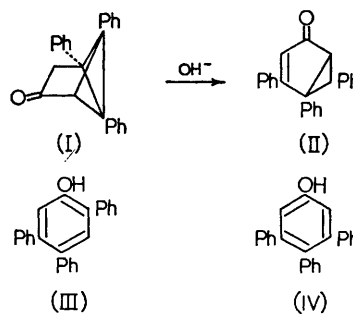
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In the presence of base 4,5,6-triphenyltricyclo[2,1,1,0^{5,6}]hexan-2-one (I)^{1a} rearranges in 70% yield to a new compound (II), C₂₄H₁₈O, m.p. 155–156°. Masamune^{1b} has reported that 5,6-diphenyltricyclo[2,1,1,0^{5,6}]hexan-2-one undergoes only deuterium exchange with sodium methoxide in deuteriomethanol and tetrahydrofuran. In contrast, when (I) was stirred at room temperature in a suspension of sodium methoxide in dioxan for 24 hr., extensive rearrangement to (II) took place. Reaction conditions for best yield involved heating under reflux in presence of sodium hydroxide in dioxan–water for 1 hr. In the infrared this compound showed a carbonyl band at 5.91 μ , in the near infrared it showed a peak at 1.68 μ typical of a cyclopropyl group,² in the ultraviolet it showed λ_{\max} . 281 m μ (log ϵ , 4.14) similar to the spectrum reported for 3-phenylcyclopent-2-en-1-one.³ Assignment of the structure (II) was also supported by the n.m.r. spectrum which showed fifteen phenyl protons centred at $\delta = 7.1$ p.p.m., one vinyl proton at $\delta = 5.9$ p.p.m. (doublet, $J = 1$), one cyclopropyl proton at $\delta = 3.1$ p.p.m. (doublet, $J = 4$) and one cyclopropyl proton at $\delta = 2.7$ p.p.m. (pair of doublets, $J = 1$, $J = 4$).

Ultraviolet irradiation of (I) in dioxan–water using a Pyrex filter gave 2,4,5-triphenylphenol

(III) as the only significant product. In contrast, (II) under similar conditions undergoes rearrangement in significant yield to 3,4,5-triphenylphenol (IV) as well as (III) and an acidic substance as yet uncharacterized. The structures of (III) and (IV) were determined by comparison (mixed melting point and infrared spectrum) with samples prepared by different routes. [The synthesis of (IV) has been reported.⁴ Compound (III) was prepared by a similar method involving base-catalyzed condensation of 3-phenylbut-3-en-2-one⁵ with benzoin to give 4-hydroxy-3,4,6-triphenylcyclohex-2-en-1-one which on heating in acetic anhydride–sulphuric acid gave the acetate of (III)].



¹ (a) A. Small, *J. Amer. Chem. Soc.*, 1964, **86**, 2091; (b) S. Masamune, *Tetrahedron Letters*, 1965, 945.

² P. G. Gassman, *Chem. and Ind.*, 1962, 740.

³ C. F. H. Allen and J. A. VanAllan, *J. Amer. Chem. Soc.*, 1955, **77**, 2315.

⁴ A. Smith, *Ber.*, 1893, **26**, 65, as modified by J. B. Garner, *Amer. Chem. J.*, 1904, **31**, 143.

⁵ W. Wilson and Z-Y. Kyi, *J. Chem. Soc.*, 1952, 1321.

Photochemical reactions similar to these have been reported. Masamune and Castellucci⁶ have found that 5,6-diphenyltricyclo[2,1,1,0^{5,6}]hexan-2-one rearranges exclusively to 2,4-diphenylphenol. Zimmerman⁷ has reported that 6,6-diphenylbicyclo[3,1,0]hex-3-en-2-one rearranges photochemically in dioxan-water to 2,3-diphenylphenol and minor amounts of 3,4-diphenylphenol as well as

acid. Our results substantiate these observations. It is of interest that compounds (I) and (II) which could pass through similar or identical intermediates in their rearrangement to phenols do not give the same mixture of products.

All new compounds have satisfactory analyses and have been characterized by the usual spectral methods.

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⁶ S. Masamune and N. T. Castellucci, *Proc. Chem. Soc.*, 1964, 298.

⁷ H. E. Zimmerman, "Mechanistic Organic Photochemistry" in W. A. Noyes, Jr., G. S. Hammond, and J. N. Pitts, Jr., Ed., "Advances in Photochemistry", Vol. I, Interscience, New York, 1963.