

ACETONE-SENSITIZED PHOTOEPIMERIZATION ABOUT UNACTIVATED
TERTIARY CARBON ATOMS

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We wish to report a facile method for the epimerization of unactivated tertiary carbon atoms in saturated hydrocarbons. Previously, epimerizations have been achieved with Lewis acid catalysts such as concentrated sulfuric acid or aluminum halides and later by the use of hydrogenation catalysts at elevated temperatures.¹ The former method is accompanied by carbonium ion rearrangements which often lead to rather complex mixtures which are difficult to analyze while the latter method requires temperatures above 250°. More recently, epimerizations have been accomplished at ambient temperature by uv irradiation with high energy (254nm) light in the presence of mercuric bromide or N-bromosuccinimide in hydrocarbon solution.² The decomposition of the mercuric bromide to an opaque black (mercury metal) deposit which coats the walls of the reaction vessel is an experimental difficulty encountered in applying this method.

We find that epimerization occurs upon irradiation with low energy (350 nm) uv light in acetone solution. Thus, irradiation of a solution of *cis*- or *trans*-decalin (40 μ l) in acetone (2ml) in a pyrex vessel with a Rayonet photochemical reactor produced mixtures containing both epimers.³

Table. Photoepimerizations of *cis*- and *trans*-decalin.

Time of Irradiation	Epimer Composition (%)	
Start	3	97
60 hr	67	33
150 hr	83	17

Start	95	5
60 hr	98	2

Similarly, a 2:8 mixture of *trans*- and *cis*-hydrindane was slowly transformed into an equilibrium mixture containing 60% *trans*- and 40% *cis*-hydrindane as shown in the figure below. This equilibrium composition is essentially the same as that previously obtained by the cationic route involving catalysis by aluminum bromide.⁴

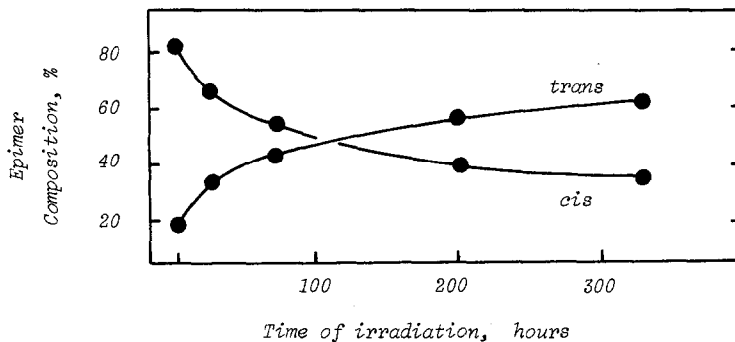
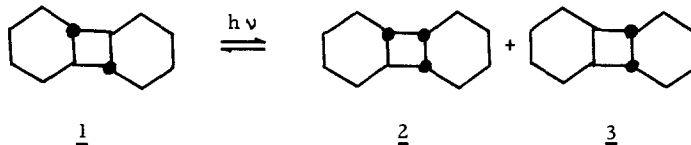


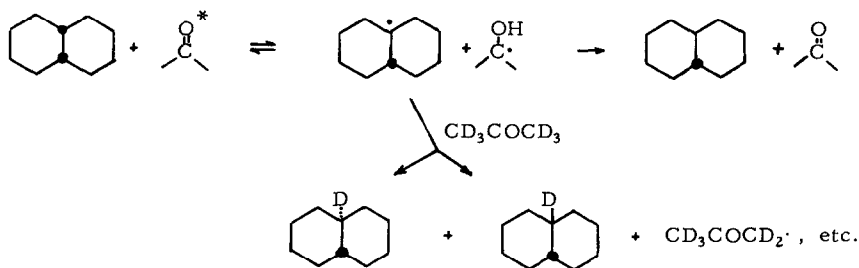
Figure. Photoepimerization of *cis* and *trans* hydrindanes in acetone.

Likewise, the cyclohexene dimer 1 gave a mixture of five isomers after irradiation for 24 hours. Three dimers were the cyclobutane epimers 1, 2, and 3 in a ratio of 79:18:3.⁵ Thus, tertiary carbon centers in four, five, and six-membered rings may be epimerized by the present method. In each case the solutions remained light and clear.



The epimerizations described above undoubtedly involve the generation of tertiary free radicals via hydrogen atom abstraction by triplet excited state acetone.⁶ Subsequent epimerization of these radicals and reversal of the hydrogen atom transfer step could account for the observed transformations. However, the intermediate tertiary radicals might alternatively abstract hydrogen from the acetone solvent. To examine the latter possibility, *cis*-decalin (97%) was irradiated in acetone-*d*₆ (96%). Hydrogen atom abstraction from the solvent in these photoepimerizations was proved by the observation of deuterium incorporation into both decalin epimers. Thus, after uv irradiation for three days, a 76:24 mixture of *trans*- and *cis*-decalin was obtained with the following

isotopic composition: *cis*-decalin 50% d⁰, 33% d¹, 12% d², 4% d³, and *trans*-decalin 28% d⁰, 46% d¹, 21% d², 5% d³.



The well-documented production of sensitizer adducts and dehydrogenation products by irradiation of hydrocarbons in the presence of ketones^{6,7} detracts from the utility of the present method of preparative synthetic applications. An advantage of the present method lies in its potential use for equilibration studies at ambient temperatures. Indeed, the method should also be applicable at reduced temperatures at which energy differences between epimers are most evident.

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3. Product mixtures were analyzed by vapor phase chromatography on a 10' x 1/8" 15% FFAP on 60/80 Chromasorb P column at 110-150°. Relative retention times on this column are *cis*-decalin = 1.32, *trans*-decalin = 1.00; *cis*-hydrindane = 1.28 *trans*-hydrindane = 1.00; (1) = 1.00, (2) = 1.22, (3) = 1.35.

4. The equilibrium composition at 27° is 61% *trans*- and 39% *cis*- hydrindane:
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5. The preparation and characterization of these epimeric cyclohexene dimers is presented in a forthcoming paper [R. G. Salomon, K. Folting, W. E. Streib and J. K. Kochi, to be published].
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