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# PHOTOSENSITIZED REACTIONS OF 1-CYCLOHEXENYL CARBINOLS

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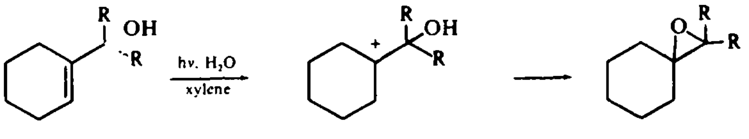
**Abstract**—Dimethyl-1-cyclohexenylcarbinol (**1a**) affords a mixture of methylcyclohexane (8%), methylenecyclohexane (2%), 1-methylcyclohexanol (5%), isopropylidenecyclohexane oxide (10%), and 2-(1-hydroxycyclohexyl)-2-propanol (20%) upon UV irradiation in aqueous t-butyl alcohol with *m*-xylene as the photosensitizer. Under the same conditions 1-cyclohexenylmethanol (**1b**) yields methylenecyclohexane oxide (trace), cyclohexylmethanol (20%), and 1-hydroxymethyl-1-cyclohexanol (25%). Possible pathways to these various products are proposed.

IN CONNECTION with a program aimed at exploring the synthetic potential of cycloalkene photochemistry,[1] we examined the photosensitized reactions of some simple cyclohexenylcarbinols **1** under conditions favoring the generation of the corresponding cyclohexyl cations **2**. We hoped that such cations would collapse to oxiranes **3** or undergo pinacol rearrangement (**2** → **4**), thereby providing novel synthetic routes to these products. Of course, cation **2** could also react with the nucleophilic solvent leading to addition products **5**, as has been observed with simple cyclohexenes and octalins.[1,2] Our findings, which we now disclose, indicate that all three of the aforementioned reactions take place with dimethyl-1-cyclohexenylcarbinol (**1a**). However ketone **4a**, the product of pinacol rearrangement, undergoes a Norrish type I cleavage[3] leading to products derivable from the resulting methylcyclohexyl radical. On the other hand, 1-cyclohexenylcarbinol (**1b**) affords mainly diol **5b** and cyclohexylcarbinol (**6**) upon irradiation under the conditions employed for the homologous carbinol **1a**. Thus, while our initial analysis has been essentially borne out, the low yields obtained in these exploratory studies make applications to synthesis appear unpromising at present. Nonetheless, we wish to report the results of our studies at this time since additional work along these lines is not foreseen in the near future and our experience with carbinols **1a** and **1b** may serve to encourage (discourage?) work on related cycloalkenylcarbinols.



**1a**: R = Me
**1b**: R = H

**2a**: R = Me
**2b**: R = H

**3a**: R = Me
**3b**: R = H

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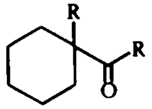
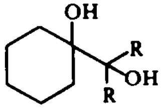
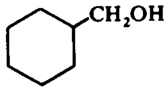


**4b**: R = H
**4a**: R = Me



**5a**: R = Me
**5b**: R = H



**6**

Irradiation[*] of carbinol **1a** in aqueous t-butyl alcohol with xylene as the photosensitizer led to a variety of products which were isolated by preparative gas chromatography and characterized by their spectral properties and through comparison with authentic samples. In this way it was possible to identify methylenecyclohexane (2%), 1-methylcyclohexanol (5%), and methylcyclohexane (8%) among the more volatile products. Small amounts of materials with retention times corresponding to 1-methylcyclohexene and methyl 1-methylcyclohexyl ketone (**4a**) could also be detected but these were not formed in sufficient quantity to isolate. A peak corresponding in retention time to isopropylidenecyclohexane oxide (**3a**) accounted for nearly 10% of the starting material, but purification could not be effected owing to the presence of an overlapping peak arising from material of undetermined structure. The remaining product (20% yield) was identified as the diol **5a**. Authentic samples of these latter products were secured as indicated in the Experimental.

Irradiation[*] of ketone **4a** in aqueous t-butyl alcohol-xylene afforded a mixture of methylenecyclohexane, 1-methylcyclohexanol, and methylcyclohexane in nearly the same ratio (1:2·7:3·3) as that obtained *via* irradiation of the carbinol **1a** under identical conditions. These findings point to ketone **4a** as the likely precursor of the more volatile products resulting from irradiation of carbinol **1a**. A reasonable pathway may be formulated whereby ketone **4a**, produced via rearrangement of cation **2a**, undergoes a Norrish type I cleavage.[3] Disproportionation of the resulting 1-methylcyclohexyl radical would afford a mixture of methylcyclohexane, methylenecyclohexane, and 1-methylcyclohexene. The latter olefin has been shown to give 1-methylcyclohexanol and methylenecyclohexane under the reaction conditions.

1-Cyclohexenylcarbinol (**1b**) afforded 1-hydroxymethyl-1-cyclohexanol (**5b**, 25%), cyclohexylmethanol (**6**, 20%), and a trace of methylenecyclohexane oxide (**3b**) upon irradiation[*] in aqueous t-butyl alcohol with xylene as the photosensitizer.

The observed reduction of 1-cyclohexenylcarbinol (**1b**) can be viewed as an ionic process[4] whereby the cation **2b** abstracts a hydride from the alcohol **1b** affording carbinol **6** and 1-cyclohexenecarboxaldehyde. The latter product would presumably undergo subsequent photochemical reactions such as addition and dimerization[5] leading to materials not detectable by the techniques employed in our study. Alternatively, the reduction could follow a free radical pathway.[6] In an effort to trace the source of H atoms in this reduction we subjected 1-cyclohexenyldideuteriocarbinol to the photochemical conditions. Unfortunately, the cyclohexylcarbinol was formed in very low yield ($\sim$1%) and readily lost $H_2O$ (HOD?) and $CD_2OH$ fragments in the mass

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[*] The irradiation was carried out with a 450 w Hanovia medium pressure Hg arc (type L) in a water-jacketed Vycor immersion well. Mixing was effected by a fine stream of $N_2$ introduced through a gas dispersion tube fitted in the bottom of the reaction vessel.

spectrometer, thereby precluding observation of a molecular ion peak. The low yield and the difficulties encountered in isolating a pure reduction product forced abandonment of this line of investigation.

## EXPERIMENTAL

2-(1-*Cyclohexenyl*)-2-*propanol* (**1a**). To a soln of 9·0 g 1-acetylcyclohexene* in 500 ml ether, 200 ml 1·6 M MeLi was added with stirring. After 2·5 hr, the soln was cautiously poured onto crushed ice, and the product was isolated by ether extraction affording 8·3 g (82%) of **1a**, b.p. 33° (0·03 mm); $\lambda_{\max}^{\text{film}}$ 2·96 (OH), 3·28 (vinyl H), 6·00 (C═C), 7·32, 8·71 and 10·86 μ; $\delta_{\text{TMS}}^{\text{CCl}_4}$ 1·22 ($CH_3$), and 5·65 ppm (vinyl H); $n_D^{26}$ 1·4813. (Found: C, 77·2; H, 11·6. Calc. for $C_9H_{16}O$: C, 77·09; H, 11·50%).

*Photolysis of* 2-(1-*cyclohexenyl*)-2-*propanol* (**1a**). A soln of 1·0 g of **1a**, 2·6 ml *m*-xylene and 0·3 g dodecane (internal standard) in 60 ml t-BuOH and 60 ml water was irradiated for 8 hr. At this point the gas chromatogram showed the virtual disappearance of **1a** and the formation of three products in the ratio 1:2·4:3·8(15% yield) at short retention times, two products in the ratio 1:1 (20% yield) at longer retention time, and one product of much longer retention time (20% yield). The first 3 peaks were isolated by preparative gas chromatography and identified as methylenecyclohexane, 1-methylcyclohexanol, and methylcyclohexane, respectively, by comparison with authentic samples. The last peak was similarly identified as diol **5a**. The middle two peaks were not sufficiently separated for individual isolation, but one of them corresponded to the oxide **3a** (peak enhancement) and the IR spectrum of an isolated mixture of the two showed all the bands of authentic oxide **3a**. The unidentified peak was not caused by 2-cyclohexyl-2-propanol.

Aliquots removed at earlier stages in the irradiation showed small peaks in the gas chromatogram attributable to 1-methylcyclohexene and the ketone **4a**. These substances could not be isolated in sufficient quantity for identification.

*Isopropylidenecyclohexane*. The prodecure of Corey *et al.*[7] was followed. The mineral oil was removed from 4·41 g NaH dispersion (51%) by thorough washing with pentane, 70 ml DMSO was added, and the mixture was heated at 70° until homogeneous. To the cooled soln was added 44·8 g isopropyltriphenylphosphonium iodide[8] in 154 ml DMSO. The mixture was allowed to reach room temp, and after 30 min it was again cooled to 0° and 3·01 g cyclohexanone in 30 ml DMSO was added. After warming to room temp, the mixture was stirred at 70° for 20 hr, cooled and treated with 105 ml water. The product was extracted with pentane and chromatographed on alumina affording 1·70 g (45%) isopropylidenecyclohexane, $n_D^{26}$ 1·4703 (lit.[9] $n_D^{20}$ 1·4720). The IR spectrum was identical to that of the published spectrum.[10]

*Isopropylidenecyclohexane oxide* (**3a**). To a soln of 0·625 g isopropylidenecyclohexane in 85 ml $CH_2Cl_2$ at 0° was added 2·30 g *m*-chloroperoxybenzoic acid. The soln was stirred at room temp for 3 hr and then washed with 10% KOH aq, dried over $MgSO_4$, and distilled affording 0·54 g (77%) of the oxide; $\lambda_{\max}^{\text{film}}$ 8·87, 11·25 and 11·89 μ; $\delta_{\text{TMS}}^{\text{neat}}$ 1·23 ppm ($CH_3$); $n_D^{26}$ 1·4510. (Found: C, 77·2; H, 11·65. Calc. for $C_9H_{16}O$: C, 77·09; H, 11·50%).

This material gave no volatile products upon irradiation under the conditions described for alcohol **1a** and ketone **4a**. After 9 hr, the gas chromatogram showed that 78% of the starting oxide was still present.

1-*Methylcyclohexyl methyl ketone* (**4a**). The method of Stork *et al.*[11] was employed. To a stirred soln of 5·0 g 1-acetylcyclohexene in 390 ml ether and 525 ml ammonia was added 0·465 g Li wire in small pieces. After 20 min, 7·5 ml MeI in 10 ml ether was slowly added. The ammonia was allowed to evaporate, the residue was treated with $NH_4Cl$ aq, and the product was extracted with ether. The crude ketone was fractionated with a 15 cm column packed with glass helices affording fractions of 1·0 g and 0·45 g, b.p. 74° (12 mm), shown to be 95% and 85% pure, respectively, by gas chromatography. The first fraction displayed the following properties: $n_D^{24}$ 1·4532 (lit.[12] $n_D^{20}$ 1·4548); $\lambda_{\max}^{\text{film}}$ 5·86 (CO), 6·90, 7·38 and 8·82 μ; $\delta_{\text{TMS}}^{\text{CCl}_4}$ 2·03 (MeCO) and 1·04 ppm (Me). The semicarbazone derivative exhibited m.p. 184–185° (lit.[12,13] m.p. 186°) after recrystallization from MeOH.

2-(1-*Hydroxycyclohexyl*)-2-*propanol* (**5a**). A soln of 1·00 g of **1a** and 1·90 g *m*-chloroperoxybenzoic acid in 40 ml benzene was stirred at 0–10° for 2 hr. The soln was washed with 10% NaOH aq, dried over

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* Aldrich Chemical Company, Milwaukee, Wisconsin.

$MgSO_4$ and distilled affording 1·06 g (95%) of the oxide, b.p. 110° (bath temp) at 18 mm; $\lambda_{max}$ 2·90 (OH), 8·63, 9·61, 10·36, 10·84, 11·38, 11·67, 11·68, 11·93 and 12·21 μ.

A 1·06-g sample of the above oxide in 125 ml of 1,2-dimethoxyethane was reduced with 1·50 g LAH at reflux for 7 hr, affording 0·96 g (90%) of diol **5a**, m.p. 72–78°. Recrystallization from hexane afforded material with m.p. 80–82° (lit.[14] m.p. 83°).

*Photolysis of* 1-*methylcyclohexyl methyl ketone* (**4a**). A soln of 0·185 g of **4a**, 2·6 ml *m*-xylene and 0·200 g dodecane (internal standard) in 60 ml of t-BuOH and 60 ml water was irradiated* for 4 hr, whereupon the gas chromatogram showed the appearance of 3 products in the ratio 1:2·7:3·3 (20% yield) and the virtual disappearance of starting **4a**. The products from a comparable but larger scale run were isolated by preparative gas chromatography and identified as methylenecyclohexane, 1-methylcyclohexanol, and methylcyclohexane, respectively, by comparison with authentic samples.

Under these conditions 1-methylcyclohexene afforded methylenecyclohexane and 1-methyl cyclohexanol in the ratio 1:2·6.

1-*Cyclohexenylmethanol* (**1b**). A soln of 6·0 g 1-cyclohexenecarboxylic acid † in 25 ml ether was added slowly to a stirred soln of 4·0 g LAH in 500 ml ether at 0°. After 5·5 hr at room temp, 8·0 ml water and 6·4 ml 10% NaOH aq were added and stirring was continued for 14 hr. The mixture was filtered and the filtrate was distilled affording 4·2 g (79%) of a 95:5 mixture (by gas chromatography) of **1b** and **6**,[15] b.p. 85–95° (12 mm), $n_D^{24}$ 1·4855 (lit.[16] $n_D^{25}$ 1·4881): $\lambda_{max}^{film}$ 3·03 (OH), 3·33 (vinyl H), 5·99 (C=C), 6·93 and 9·90 μ; $\delta_{TMS}^{CCl_4}$ 3·83 (—$CH_2O$—), and 5·58 ppm (vinyl H).

Photolysis of 1-*cyclohexenylmethanol* (**1b**). A soln of 1·50 g of the 95·5 mixture of **1b** and **6**, 2·1 g *m*-xylene, and 0·75 g dodecane (internal standard) in 60 ml t-BuOH and 60 ml water was irradiated* for 6 hr, whereupon the gas chromatogram showed the appearance of 2 products in 20% and 25% yield and a trace of material whose retention time corresponded to that of methylenecyclohexane oxide. The major products were isolated by gas chromatography and identified as **6** and **5b**[17] by comparison with authentic samples.

Essentially the same results were obtained upon irradiation of a purified (gas chromatography) sample of **1b**.

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* See footnote p. 2.

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