

**Anti-Markovnikov Addition of Nucleophiles to a
Non-conjugated Olefin *via* Single Electron Transfer Photochemistry**

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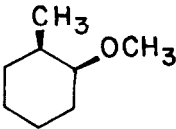
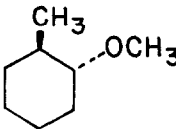
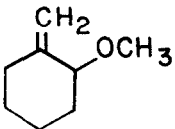
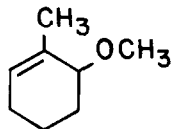
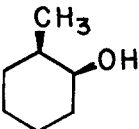
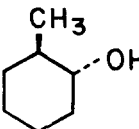
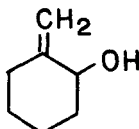
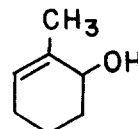
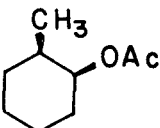
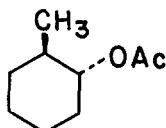
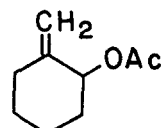
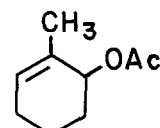
Abstract: Nucleophilic solvent has been added regiospecifically in an anti-Markovnikov manner to a simple non-conjugated olefin, 1-methylcyclohexene, through single electron transfer induced photochemistry using the 1-cyanonaphthalene - biphenyl pair for achieving photooxidation.

Although photoinduced additions of nucleophiles to derivatives of styrene and stilbene are well known,¹ relatively little is known about the photoinduced addition of nucleophiles to simple non-conjugated olefins. Kropp has described the addition of ethanol to 2,3-dimethyl-2-butene *via* direct irradiation and suggested the presence of an excited Rydberg state.² Lewis and DeVoe examined the photosensitized addition of methanol to this same olefin, albeit in low yield.³⁻⁵

Our extensive experience with the addition of nucleophiles to highly strained carbon-carbon single bonds *via* single electron transfer (SET) photochemistry⁶ suggested to us that simple olefins, such as 1-methylcyclohexene, should have sufficiently high energy highest occupied molecular orbitals (HOMO) that they would readily donate an electron to a sufficiently strong excited state oxidant. To test this hypothesis, we utilized 1-methylcyclohexene (**1**),⁵ which has an $E_{1/2}^{ox} = 1.77$ V vs SCE, as our substrate and 1-cyanonaphthalene (1-CN, **2**), which has an $E_{1/2} = 1.84$ V as an oxidant in its excited state, as our SET photosensitizer. In exploratory studies, a 40:60 solution of methanol-acetonitrile containing **1** and 55 mol % of 1-CN (**2**) was irradiated for 45 h in a Pyrex vessel with sixteen 3000 Å light bulbs in a Rayonet photoreactor equipped with a merry-go-round apparatus. GLC analysis of the crude product showed the presence of 21% of **3**, 20% of **4**, 4% of **5** and 3% of **6**.⁷⁻¹¹ Addition of 50 mol % of biphenyl to the solution as a cosensitizer¹⁸ resulted in a decrease in irradiation time from 45 h to 18 h and gave isolated yields of 21%, 19%, 4%, and 3% for **3**, **4**, **5**, and **6**, respectively.¹⁹

Table 1 gives a comparison of the products formed in 40:60 methanol-acetonitrile, 30:70 water-acetonitrile, and 40:60 acetic acid-acetonitrile. As can be seen from the Table, the overall yields

Table 1. Yield of the Nucleophilic Photoaddition Products Obtained in the Irradiation of 1-Methylcyclohexene (**1**) with 1-CN and Biphenyl as a SET Photosensitizer Combination.

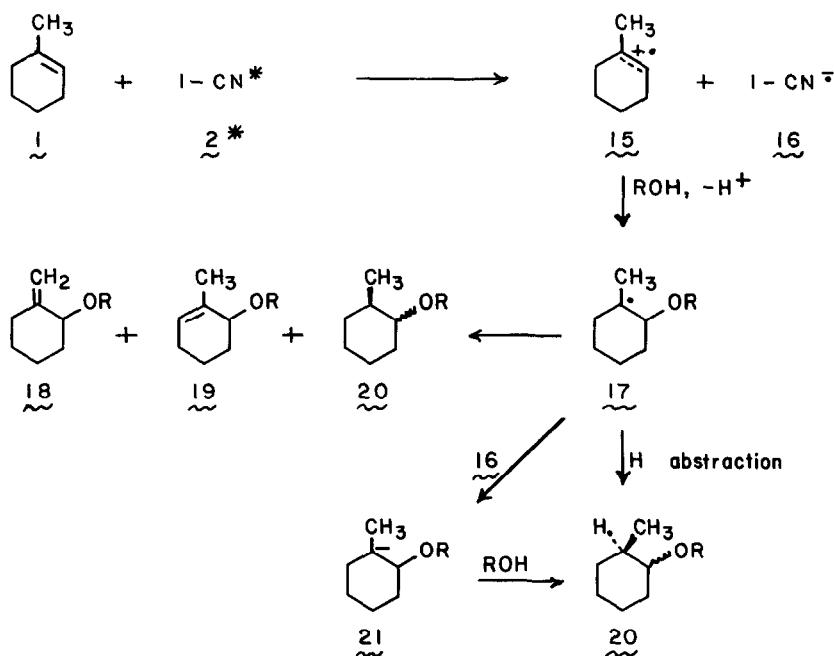
Solvent	Time (Min.)	Products and Yields ^a			
CH ₃ OH-CH ₃ CN	280 ^b	 3 (22%) ⁸	 4 (20%) ⁹	 5 (5%) ¹⁰	 6 (3%) ¹¹
H ₂ O-CH ₃ CN	110	 7 (22%) ¹²	 8 (15%) ¹³	 9 (4%) ¹⁴	 10 (2%) ¹⁴
CH ₃ CO ₂ H-CH ₃ CN	300	 11 (14%) ¹⁵	 12 (22%) ¹⁵	 13 (1%) ¹⁶	 14 (2%) ¹⁷

(a) GLC yields vs an internal standard following isolation of the crude product mixture. (b) The 4.7 h listed here is considerably shorter than the 18 h listed in the text due to the smaller scale on which this reaction was run. Yields were similar on the two different scales (28 mg vs 4.1 g of **1**).

of products resulting from SET photosensitized nucleophilic addition of solvent to **1** varied from 50% for methanol to 39% for acetic acid. In general, the product ratios were very similar.

The use of Pyrex precluded any direct excitation of **1**. It is clear that **2** was the initially excited species. Single electron transfer from **1** to excited state **2** would produce the cation radical - anion radical pair, **15** and **16**. Nucleophilic attack of solvent on **15**, followed by proton loss should yield **17**. The

formation of **18** and **19** can be accounted for on the basis of a radical disproportionation reaction which would require the formation of an amount of **20** comparable to the combined yields of **18** and **19**. It is obvious that the majority of **20** must come from some other mechanistic path. The two most logical routes are through **17** *via* hydrogen abstraction from solvent or from the protonated form of the anion radical of 1-CN to give **20** directly. A less likely mechanistic path would involve back electron transfer from **16** to **17** to produce **21** followed by protonation of **21** to produce **20**.



The extremely clean anti-Markovnikov addition of nucleophilic solvents to **1** under our reaction conditions can be contrasted to both the direct irradiation and photosensitized Markovnikov addition of solvents to **1**, which have been shown to occur *via* a *trans*-cyclohexene derivative.²¹ Although our yields are moderate, we feel that the SET photosensitized anti-Markovnikov additions described herein may find considerable synthetic utility.

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 19. GLC yields for this reaction vs internal standards were 22%, 20%, 5%, and 3% for **3**, **4**, **5**, and **6**, respectively. This indicates that only very minor losses of product occurred during the isolation and purification procedure. Approximately 50% of the starting 1-methylcyclohexene was unaccounted for in this reaction. The loss of photosensitizer (1-CN) suggests that complex photoadducts may be formed from **1**, 1-CN, and the solvent.²⁰
 20. A related addition of methanol to **1** in the presence of dicyanobenzene has been studied by D. R. Arnold and coworkers. We thank Professor Arnold for sharing his results with us prior to publication.
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