

PHOTOREACTIONS OF SILYL ENOL ETHERS OF α -TETRALONE AND α -INDANONE WITH ELECTRON DEFICIENT OLEFINS; THE PHOTO-MICHAEL REACTION¹⁾

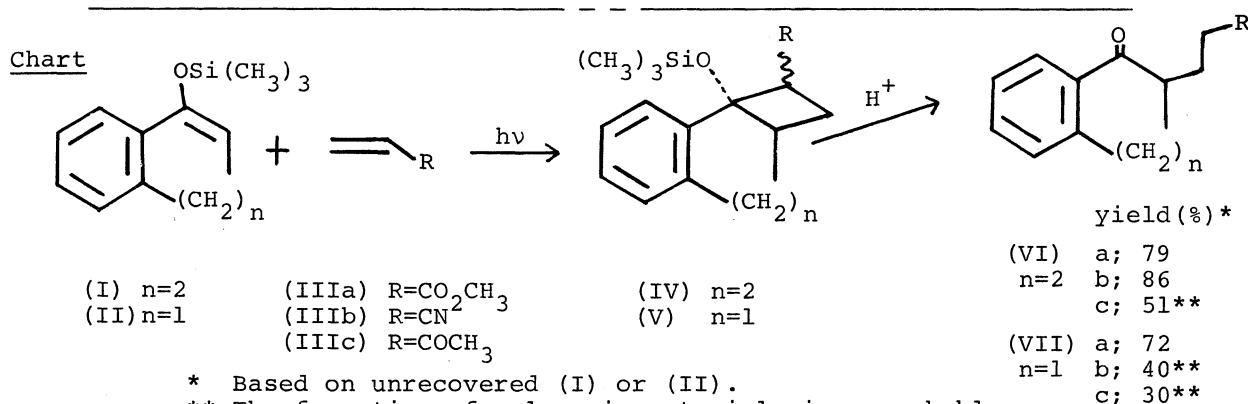
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Michler's ketone-sensitized photoreactions of silyl enol ethers of α -tetralone and α -indanone with electron deficient olefins gave photocycloadducts, hydrolyses of which lead to the Michael adducts of the corresponding ketones in good yields, under very mild conditions.

The Michael reaction is a well-known synthetic method for bond formation between activated carbons and Michael acceptors under basic conditions.²⁾ However, difficulties are encountered on selective monoalkylation and efficient alkylation of some compounds such as α -tetralone.^{2,3)} As part of our investigation on photocycloaddition reactions⁴⁾ and application of silyl enol ethers as the synthetic equivalent of enols,⁵⁾ we report here photoreaction of silyl enol ethers of α -tetralone and α -indanone with some Michael acceptors which we call the photo-Michael reaction.

The trimethyl silyl enol ethers (I) and (II) are readily prepared from the corresponding ketones.⁶⁾ Irradiation of a benzene solution containing (I) and methyl acrylate (IIIa) in the presence of Michler's ketone⁷⁾ gave cycloadduct (IVa)



in ca. 80 % yield (m/e 304(M^+), 218(100 %), and 73(88 %), ν_{max} 1735(C=O), 1253, 843, and 761 cm^{-1} (Si(CH₃)₃). Probably (IVa) is a mixture of two isomers since the NMR spectrum shows two methyl signals at δ 3.21 and 3.62 in a ca. 1:2 area ratio. Cycloadduct (IVa) was readily hydrolyzed by an aqueous methanolic solution of hydro-

chloric acid (0.5 N) at room temperature to give Michael product (VIa) in excellent yield (> 90 %). The product was isolated in analytically pure form by distillation, and converted to its 2,4-dinitrophenylhydrazone (mp 196-198 °C(dec.)). More conveniently, (VIa) was obtained in similar net yield even by direct hydrolysis of the reaction mixtures without isolating (IVa). Similarly, irradiation of (II) and (IIIa) and the subsequent hydrolysis gave again the Michael adduct of α -indanone (VIIa) in good yield. This method is available for the preparation of Michael adducts of (I) and (II) with acrylonitrile (IIIb) and methyl vinyl ketone (IIIc); yields are listed in Chart. These photoreactions were sensitized by triplet sensitizers such as Michler's ketone, acetophenone, and benzophenone, of which Michler's ketone was found to be the most favorable, since formation of polymeric materials was least.

Synthetic advantages of this method would be provided by (1) neutral conditions of the photoreaction, (2) efficient hydrolysis of the photoadducts by either acids or bases even under mild conditions and (3) selective monoalkylation. Usual Michael reactions under basic conditions frequently tend to afford various by-products by self-condensation reactions, the Michael reaction followed by aldol reaction and so on,²⁾ though some improved methods have been reported.⁸⁾ Moreover, alkylation of α -tetralone via its enamines has been reported to proceed in poor efficiency owing to steric inhibition of resonance.³⁾

It should be noted that an important point of this method is regioselectivity of the photoaddition which would be determined by both steric and electronic factors of 1,4-biradical intermediates,⁹⁾ and that silyl enol ethers in the electronically excited state can be also used as the synthetic equivalent of enols.¹⁰⁾

REFERENCES AND FOOTNOTES

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- 9) In all cases, compounds assignable to cyclobutanols which arise from cycloadducts of opposite photoaddition were detected in hydrolyzed reaction mixtures by close analyses of the IR and NMR spectra, though yields were less than 10 %.
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