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Electron Transfer Mediated Photoreductions of α,β-Unsaturated Ketones[1]

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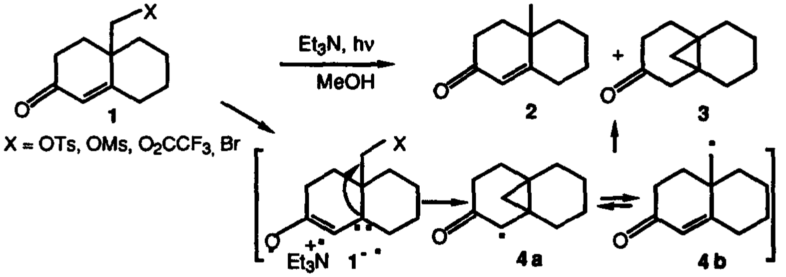
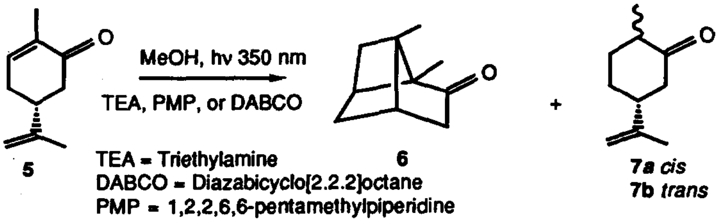
ABSTRACT: The photoreduction of α,β-unsaturated ketones with triethylamine-alcohol solutions yields dihydro- and pinacol products. With 2 to 3 M triethylamine in methanol, the photoreduction occurs with good efficiency. Protonation by methanol of the semi-enone intermediate occurs at the β-carbon to yield the dihydro product.

The photoreactions of α,β-unsaturated ketones with tertiary amines have been reported[2] to proceed by a single electron transfer (SET) mechanism. The intermediacy of the nucleophilic radical anion or semi-enone ($1^{-\cdot}$) was established through an investigation of the photochemistry of a series of tetralones with tertiary amines in alcohols. Only two products were obtained: 2 (97%) and 3 (3%) (Eq. 1).[3]



...Eq. 1

A mechanistic study of this reaction suggested that the semi-enone ($1^{-\cdot}$) reacted through an internal nucleophilic displacement generating the cyclopropylcarbinyl radical **4a** which rapidly opens to form neopentyl radical **4b**. The equilibrium mixture of **4a** and **4b** reacts either by hydrogen abstraction or by a second electron transfer followed by protonation to give 2 and 3. Based on these results, we anticipated that photoreduction of 1 by protonation of the semi-enone would be the principal reaction in the absence of a good leaving group at the 10-methyl position. We report here our results on the photochemistry of several α, β -unsaturated ketones with tertiary amines in methanol.



TEA = Triethylamine
DABCO = Diazabicyclo[2.2.2]octane
PMP = 1,2,2,6,6-pentamethylpiperidine

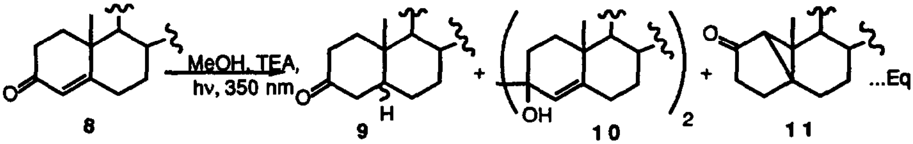
...Eq 2.

A key feature of this study is the use of methanol as the solvent and proton source. For example, when carvone (5) was irradiated at 350 nm with a series of tertiary amines, both carvonecamphor (6) and dihydrocarvone (7) were formed. Increasing the amine concentration from 0.5 M to 3 M (triethylamine, TEA) increased the ratio of

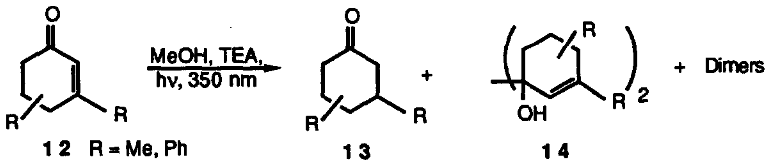
7:6 from 1:1 to 6:1. Both the carvone disappearance and the dihydrocarvone appearance efficiencies displayed parabolic dependence on the TEA concentration over the range from 0 to 7 M. At higher TEA concentrations, quenching and other reactions such as amine-enone adduct formation intervene. In the concentration range between 0.1 M and 3.0 M TEA, a linear double reciprocal relationship with a slope of 1.2 M^{-1} was determined which is in accord with a bimolecular amine-triplet enone reaction pathway.

The reduction of carvone to dihydrocarvone is quenched by piperylene with a Stern-Volmer slope of 123 M^{-1}. Likewise, carvonecamphor production is quenched with a Stern-Volmer slope of 35 M^{-1}. Lifetimes of 6.8×10^{-9} sec and 1.9×10^{-9} were calculated for the two precursors of 6 and 7, respectively [if $k_q = k_{diff} \approx 1.8 \times 10^{10}$ M^{-1} s^{-1} (for methanol)].[4] From the quenching studies, the precursor of 6 was assigned to the triplet of 5[5] whereas the precursor to 7 was most likely a triplet exciplex.[2d, 6]

Photoreductions of other cyclic enones gave similar results. A series of octalones (8), e.g., phenanthrone, Wieland-Miescher ketone, cholestenone, testosterone and 9-methyl-3-octalone photolyzed in TEA-methanol mixtures (Eq 3) gave pinacols (10) as the major products typically formed in 85-90% yields. The reduced products (9) were the minor products formed in 5-10% yields along with small amounts of the known photorearrangement products, e.g., lumiketones (11).



...Eq 3.



...Eq 4.

Monocyclic enones (12), *viz*, isophorone and 3,4-diphenylcyclohexenone, on photolysis in TEA-alcohol also gave pinacols 14 in >80% yields and minor yields of dihydro product. 2-Cyclohexenone and 4,4-dimethylcyclohexenone gave a mixtures of [2+2] dimers in addition to the pinacols as the major product and reduced product was obtained as the minor product (<10%). Analysis of variety of solvents including methanol, 2-propanol, tetrahydrofuran, acetonitrile, and benzene established that photoreduction was most efficient in methanol. Triethylamine was found to be the most efficient tertiary amine in affording the photoreduction.

A labeling study was undertaken to determine the origin of β-hydrogen in the carvone study since the reduction in methanol-tertiary amine mixtures could occur either by protonation of the semi-enone or by direct hydrogen abstraction by the β-carbon[7] as outlined in Scheme 1. A series of deuterated methanols (CH_3OD, CD_3OD and CD_3OH) and a deuterated amine, 2,2,6,6-tetramethyl-1-trideuteromethylpiperidine (PMP N-CD_3), were employed and the products were analyzed by GC-MS. Incorporation of five deuterium atoms in dihydrocarvone was observed for both CD_3OD and CH_3OD. Three of the five deuterium atoms were exchangable under the reaction conditions (2.3-2.5 ppm, Figure 1). A fourth deuterium (1.0 ppm, ^2H NMR, Figure 1) was incorporated on the α-methyl group by a reversible 1,4-hydrogen abstraction. The remaining deuterium atom was incorporated at the β-position of the semi-enone oriented either in an axial or equitorial configuration in a 3:1 ratio (1.35 ppm, 3a, and 2.1 ppm, 3e, equitorial). No deuterium incorporation was observed for CD_3OH or PMP (N-CD_3). Figure 1 shows the assignment of each deuterium atom of *trans*-dihydrocarvone by ^1H and ^2H NMR.

Scheme 1. Potential Sources of β-Hydrogen

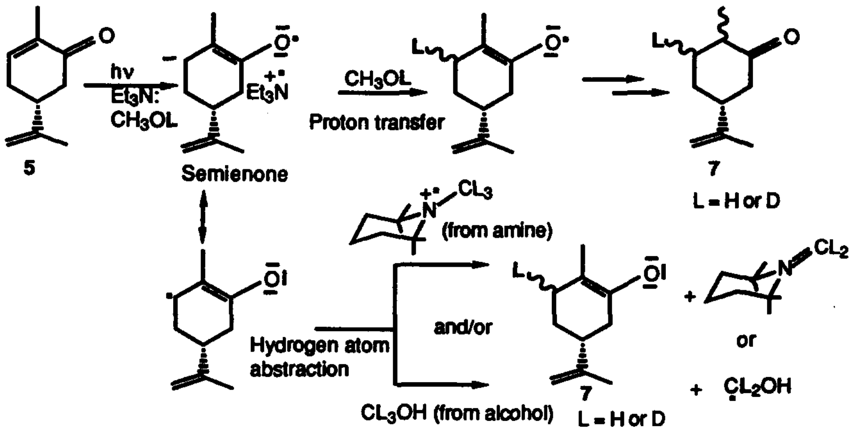


Figure 1. ^1H and ^2H NMR Spectrum of *trans*-Dihydrocarvone

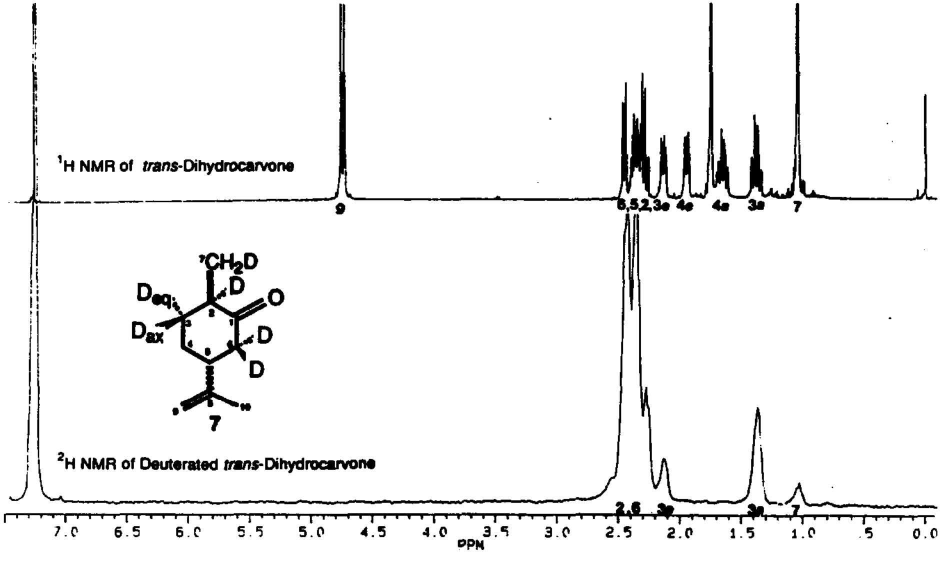


Table 1. Quantum Efficiencies for Carvone as a Function of Deuterated Solvent ([TEA]= 0.7M)

Solvent	$10^3\Phi_{dis}(5)$	$10^3\Phi_{app}(7)$	$10^3\Phi_{app}(6)$
CH_3OH	21 (±2)	5.0 (±.5)	1.5 (±.6)
CH_3OD	20 (±3)	3.2 (±.3)	1.8 (±.4)
CD_3OD	21 (±2)	3.2 (±.3)	1.8 (±.2)
CD_3OH	22 (±3)	5.4 (±.4)	1.6 (±.6)
Solvent Isotope Effect*	Φ_H/Φ_D	Φ_H/Φ_D	Φ_H/Φ_D
CH_3OH/CH_3OD	1.05	1.56	0.83
CH_3OH/CD_3OH	0.95	0.93	0.94

* Error limit was ± 0.15

Isotope effects on the quantum efficiencies in deuterated solvents (Table 1) indicated that the formation of dihydrocarvone (7) is *ca.* 1.6 times slower in methanol O-*d*. This primary kinetic solvent isotope effect indicates that the proton transfer transition state is very "reactant-like".[8] In contrast, a kinetc isotope effect of *ca.* 1.0 was observed for the disappearance quantum efficiencies of carvone and appearance efficiencies of carvonecamphor.

In general, it appears that irradiation of α,β-unsaturated ketones by tertiary amines in methanol produces mixtures of β-protonated and pinacol coupling reduction products. Conditions necessary to control the partitioning of the two pathways are currently under investigation.

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