Investigations on photochemistry of $\alpha$-allenic ketones: Interception of a polarized excited state through methanol addition

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$n\rightarrow\pi^*$ Excitation (pyrex glass reactor) of $\alpha$-allenic ketones leads to population of a polarized excited state of allenic moiety which has been intercepted, in high turnover, by methanol addition.

Due to its peculiar nature the allenic chromophore and its electronic excited states have been considerably investigated and continue to draw the attention of both theoreticians and experimentalists. Though photochemistry of a variety of substituted allene including that of a homoconjugated allenic ketones has been investigated and its peculiarities have been reported, there is no report available on excited state behavior of $\alpha$-allenic ketones, which apparently possess an interesting chromophore having an allenic moiety in conjugation with a carbonyl function. In continuation of our investigations on allene chemistry, we have presently investigated the excited state behaviour of conjugated allenic ketones 1a-e. These molecules remain virtually untransformed on irradiation in aprotic solvents like benzene, acetonitrile, however, on irradiating their methanolic solution (pyrex glass reactor), they undergo solvent addition leading, stereoselectively, to (E)-4-methoxy-3-penten-2-one and its 5-aryl derivatives (2a-e, Scheme I).

Penta-3,4-diene-2-one (1a) was prepared according to literature method and preparation of 1b-e has been recently reported. Irradiation of methanolic solution of allenic ketones 1a-e under an oxygen free dry atmosphere afforded enol ethers 2a-e which have been characterized spectrscopically (IR, $^1$H and $^{13}$C NMR, Mass). The presence of an $\alpha,\beta$-unsaturated carbonyl moiety was inferred from the IR spectra and it was corroborated by $^{13}$C NMR spectra. The assigned geometry is based on $^1$H nOe measurements in case of 2a,b and aromatic solvent induced shifts (ASIS).

The obtained mode of photoaddition is different from reported ground state nuleophilic and $HX$ ($X =$ Cl, Br etc.) additions to conjugated allenic ketones; the latter additions involve only the $\pi$ bond which is conjugated with carbonyl function. Mechanistically, the observed photoaddition of methanol to allenic ketones can be rationalized through involvement of a polarized excited state (A, Scheme II); such non-vertical, polarized excited states of allenes have been postulated and are reportedly involved in phototransformations of allenes. It is interesting to observe that in the present case the reaction, probably is initiated by an initial $n\rightarrow\pi^*$ excitation ($\lambda > 295$ nm), as it has been carried out in a pyrex glass reactor. It must be mentioned here that $\pi\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$ transitions of phenyl substituted allenes also appear above 300 nm, however, they have very low values of extinction. The inferences regarding the initiation of phototransformation are also corroborated by the observed addition of methanol to 1a which lacks phenyl substituent and whose $\pi\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$ transitions are located at 255 nm. The reported phototransformations of allenes including those of phenyl substituted allenes have been carried out in quartz glass photoreactors by exciting mainly at 254 nm and emanate from vertical $\pi\rightarrow\pi^*$ excitations. Whether the proton addition occurs directly at C-5 or it is first attached to oxygen and then transferred to C-5 has not been ascertained. In aprotic solvents (benzene, acetonitrile) these molecules probably
undergo rotational relaxation (decay of excited state)\(^6\) and display high photochemical stability.

Though the reaction is initiated by \(n \rightarrow \pi^*\) excitation of the carbonyl function, which relaxes to a polarized excited state of allenic moiety, the multiplicity of the involved excited state could not be unequivocally established. Involvement of a polarized triplet state of allenic moiety has been established in the photoaddition of acetic acid to phenyl substituted allenes, by irradiating at 254 \(\text{nm}\),\(^2\) however, in present investigations the quenching experiments with triplet sensitizer (xanthone) did not show any observable effect on either reaction time or product yield. In the present case the reaction apparently proceeds through a singlet or both singlet and triplet excited states.

It is interesting to observe that the results can also be interpreted as (a) an intramolecular photosensitization of allenic moiety by an excited carbonyl function (b) as an intramolecular photoreduction of \(\alpha,\beta\)-unsaturated carbonyl system by electron transfer from the orthogonal \(C_1-C_3-\pi\) bond followed by a rotation around \(C_1-C_2\) bond leading to (A). It may be mentioned here that in the control dark experiments at ambient temperature these ketones undergo extensive deterioration within few days. Though this deterioration is checked at low temperature (-10°C), the photolysis at low temperature gives improved yields of methanol addition products.

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References and Notes


7. Irradiation of methanolic solution (250 mL) of allene ketones \(1\text{a-e (1.60 mmole) were carried out in an immersion well photoreactor with a 400 Watt medium pressure mercury arc for 5-17 hr (Scheme I)}\); dry oxygen free nitrogen was bubbled for 30 min prior to start of irradiation and continued during irradiation period. After the starting ketone was consumed (TLC) the solvent was removed in vacuo and products were purified by column chromatography over silica gel (60-120 mesh, eluent CH\(_2\)Cl\(_2\)/Pet ether 1:5). Though the obtained products are enol ethers of known \(\beta\)- diketones we could not find the spectroscopic data or any earlier report on
such compounds, therefore the spectroscopic data has been included for some products.

2b. Colorless oil (72%); IR (neat): 1684, 1590 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 200 MHz): 2.21 (s, 3H, CH$_3$), 3.64 (s, 3H, OCH$_3$), 4.09 (s, 2H, -CH$_2$), 5.48 (s, 1H, olefinic H), 7.15-7.31 (m, 5H, Ar-Hs). $^1$H NMR (CD$_2$Cl$_2$, 200 MHz): 1.96 (s, 3H, CH$_3$), 2.88 (s, 3H, OCH$_3$), 4.31 (s, 2H, -CH$_2$), 5.94 (s, 1H, olefinic H), 7.07-7.22 (m, 3H, Ar-Hs), 7.53 (d, 2H, $J=7.6$ Hz, Ar-Hs); $^1$C NMR (CDCl$_3$, 50 MHz): 32.21, 37.62, 55.49, 99.28, 126.4, 128.2, 129.1, 137.7, 173.4, 195.9; MS: $m/z$ 192 (M$^+$+2, 3), 191 (M$^+$+1, 20), 190 (M$^+$, 100).

2c. Colorless oil (70%); IR (neat) 1684, 1599 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 200 MHz): 2.20 (s, 3H, CH$_3$), 2.33 (s, 3H, CH$_3$), 3.57 (s, 3H, OCH$_3$), 4.04 (s, 2H, CH$_2$), 5.45 (s, 1H, olefinic H), 7.02-7.20 (m, 4H, Ar-Hs). $^1$C NMR (CDCl$_3$, 50 MHz): 21.1, 32.2, 37.2, 55.5, 98.2, 129.3, 129.4, 134.9, 137.0, 173.5, 196.1; MS: $m/z$ 205 (M$^+$+1, 15), 204 (M$^+$, 78).


9 For substituted allenes wherein two $\pi$ bonds lose degeneracy, the $\pi \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$, transitions which are electric dipole forbidden and magnetic dipole allowed, resembling $n \rightarrow \pi^*$ transitions of carbonyl compounds are generally obtained in the region 220-320 nm.