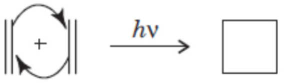
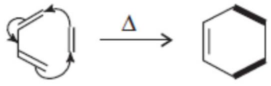
CYCLOADDITION REACTION

A cycloaddition is a reaction in which two unsaturated molecules undergo an addition reaction to yield a cyclic product.



Loss of two π bonds and gain of two σ bonds

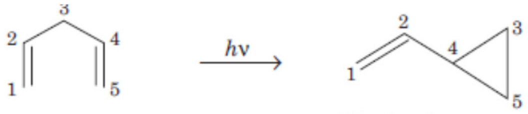


Loss of two π bonds and gain of two σ bonds. Formation of σ bonds at the end of the two components.

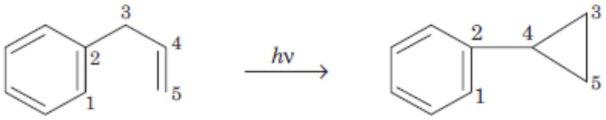
Formation of cyclic product takes place at the expense of one π (*pi*) bond in each of the reacting partner and gain of two σ (*sigma*) bonds at the end of the both components having π (*pi*) bonds. Thus, in this reaction there is loss of two π (*pi*) bonds of the reactants and gain of two σ (*sigma*) bonds in the product.

Di-π-METHANE (DPM) REARRANGEMENT

The most remarkable photochemical reaction of nonconjugated dienes is the di-π-methane rearrangement. This rearrangement is given by dienes having π (*pi*) system separated by an sp^3 hydridised carbon atom *i.e.,* 1, 4-pentadienes. The rearrangement is also given by 3-phenylalkenes in which one of the double bonds is replaced by benzene ring. di-π-methane rearrangement is also known as **Zimmerman rearrangement** or **Zimmerman di-π-methane rearrangement**. Irradiation of the substrate induces rearrangement to a vinylcyclopropane or phenylcyclopropane derivative.

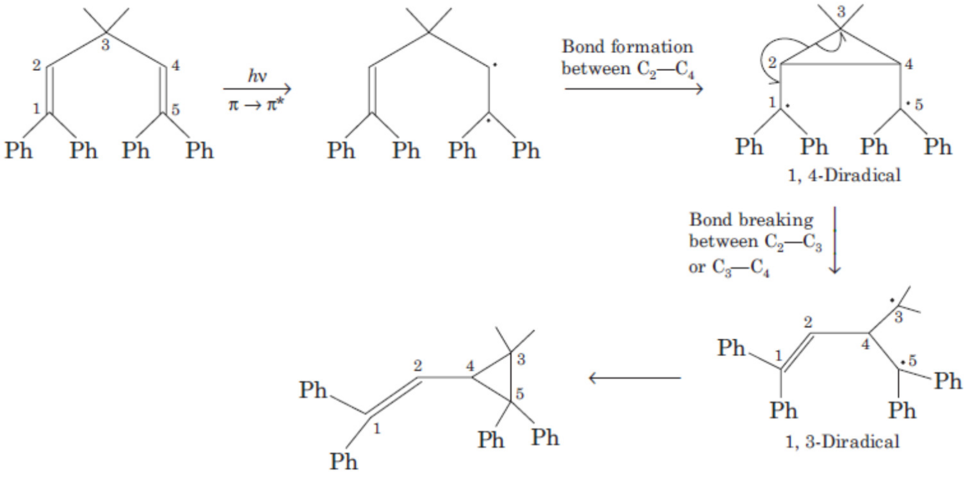


Vinylcyclopropane

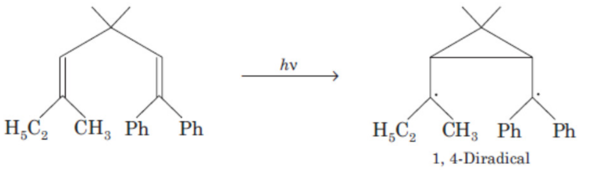


Phenylcyclopropane

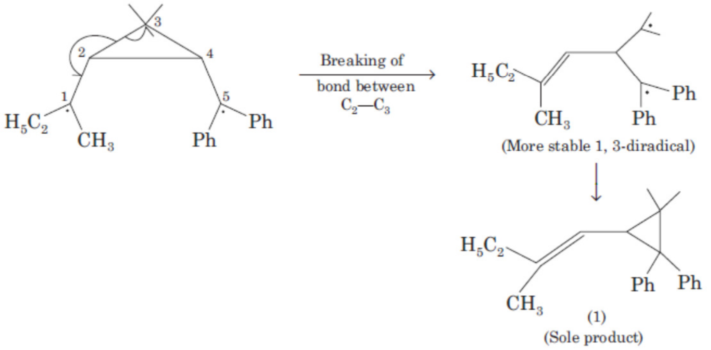
In actual practice the reaction is represented as one involving a 1, 4 and 1, 3-diradical intermediates in case of 1, 4-pentadiene since it is easier to follow the various steps necessary for the rearrangement.



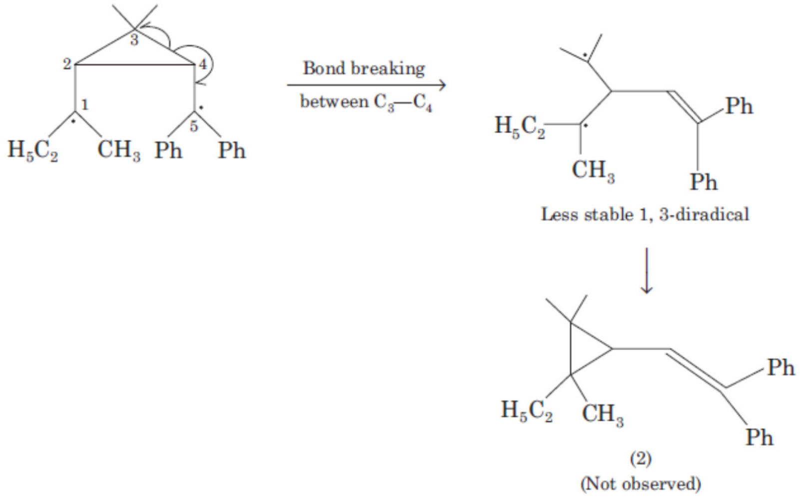
The reaction path that would involve the more stable diradical is always followed.



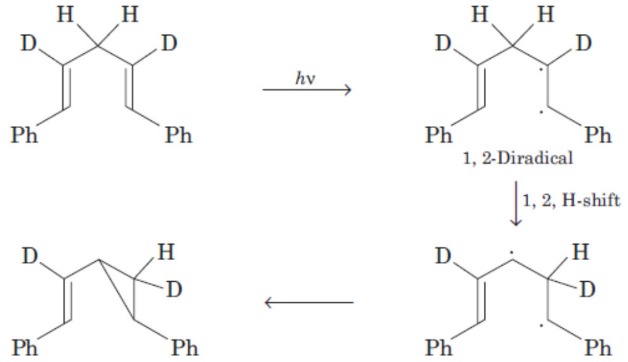
Route-*a*



Route-*b*

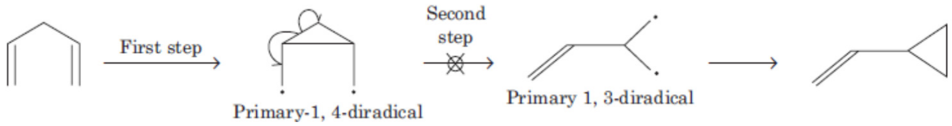


When the central *sp*3 carbon (C 3—carbon) is unsubstituted, the *di*-π-methane rearrangement mechanism becomes less favourable. In such cases the route is the 1, 2-shift and closure to a three membered ring.



Some more examples for DPM:

1.



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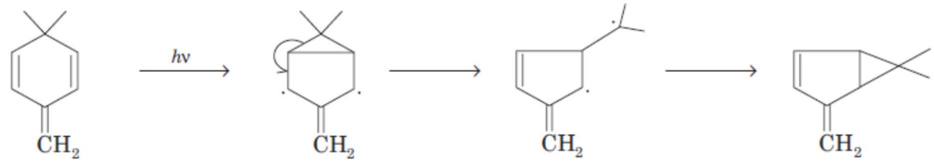
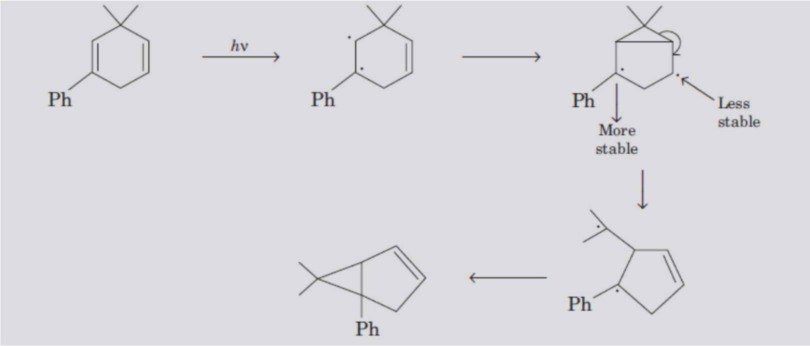


(1)

3.



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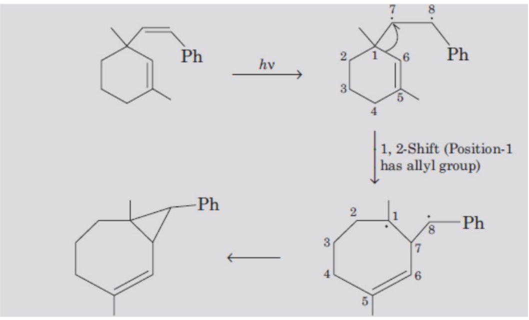

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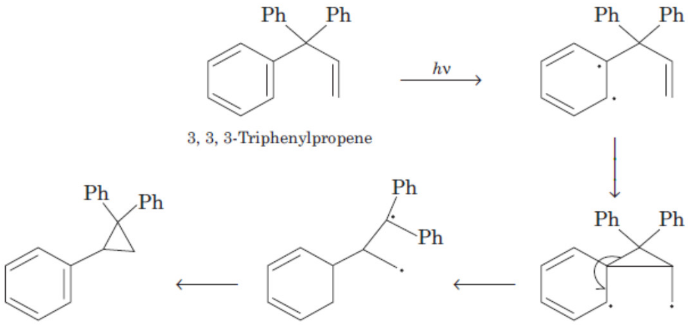

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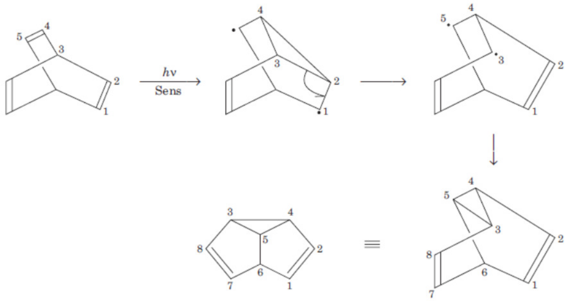
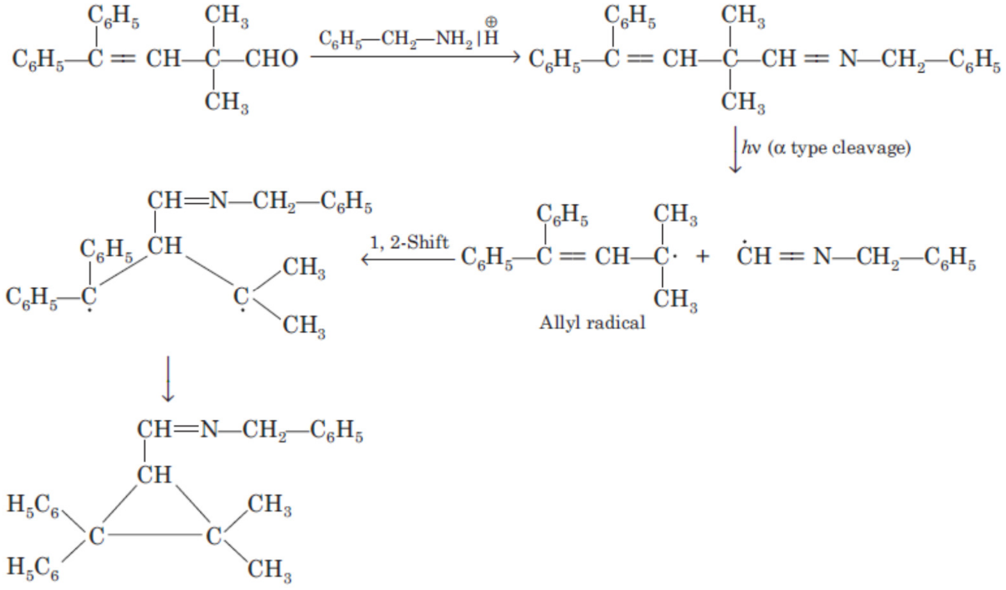
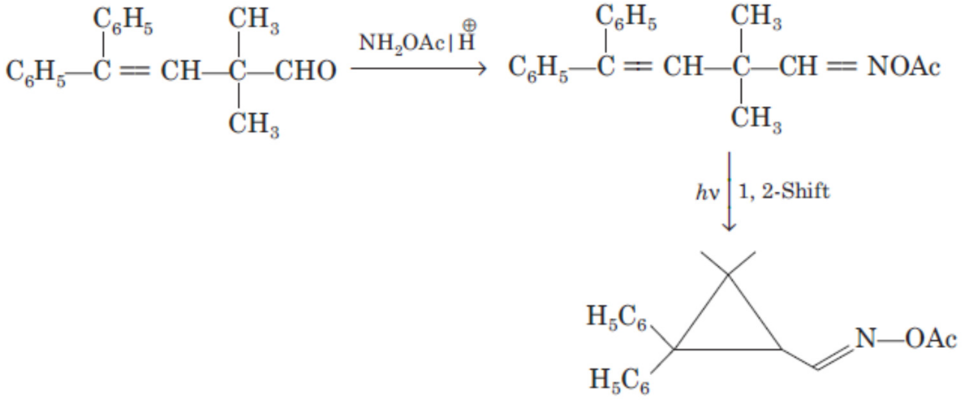


Aza-Di-π-METHANE REARRANGEMENT

1, 2-Acyl shift is given only by β□□Y-unsaturated ketones. This rearrangement is not given by aldehydes. The failure of aldehydes to undergo 1, 2-acyl shift (*i.e.,* oxa-di- π –methane rearrangement) can be overcome by conversion of the aldehyde to an imine. Thus when aldehyde is converted to the imine and irradiated under sensitised conditions, the normal cyclopropane forming process takes place. The formation of the cyclopropane by this path is known as aza di-π-methane rearrangement.



A similar path has also been shown to be involved with the oxime acetate.



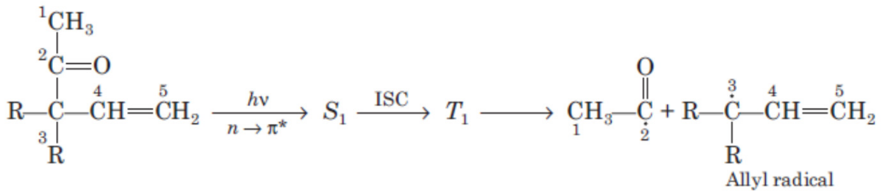
Oxa-Di-π-methane rearrangement: Di-π-methane rearrangement given by β, γ unsaturated ketone is known as oxa-di-π-methane rearrangement.

PHOTO REARRANGEMENTS OF β, γ-UNSATURATED KETONES

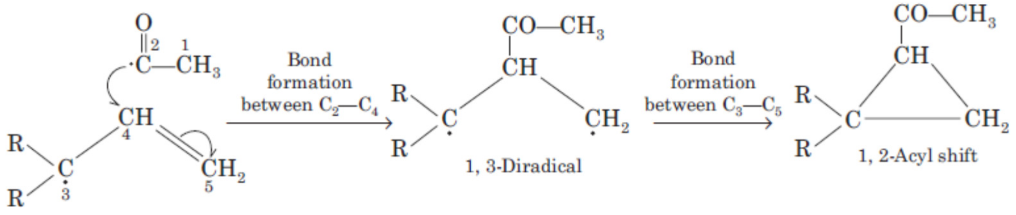
The rearrangements are 1, 2-acyl shifts (oxa-di-π-methane rearrangements) which occur from the lowest triplet state of $n \rightarrow \pi^*$ transition and 1, 3-acyl, shifts which occur from direct irradiation from the S_1 or T_2 ($n \rightarrow \pi^*$) state with formation of an acyl-alkyl radical pair.

Mechanism of 1, 2-Acyl Shift

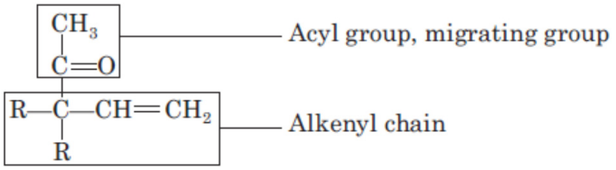
In this rearrangement the primary step is the α-cleavage which leads the formation of acyl radical and allyl radical.



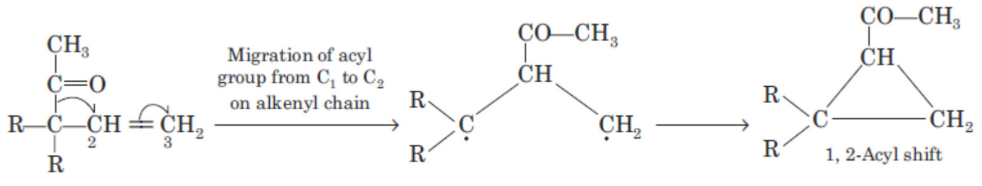
In the next step C_2—C_4 bond formation takes place between acyl radical and allyl radical which leads to the formation of 1, 3-diradical.



For 1, 2-acyl shift the substrate can be divided into two parts, the alkenyl chain and the acyl group which is migrating group.

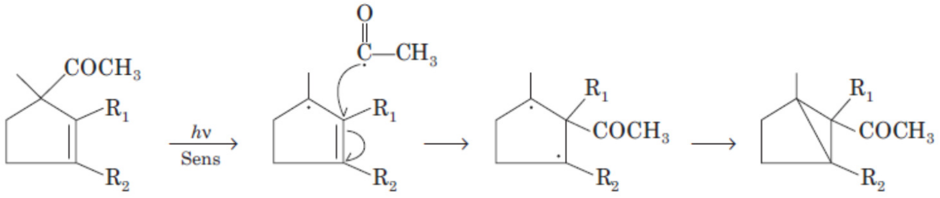


1, 2-Acyl shift in short can be represented as follows:

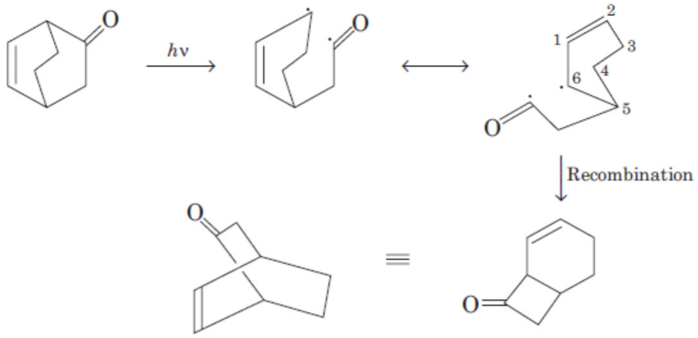


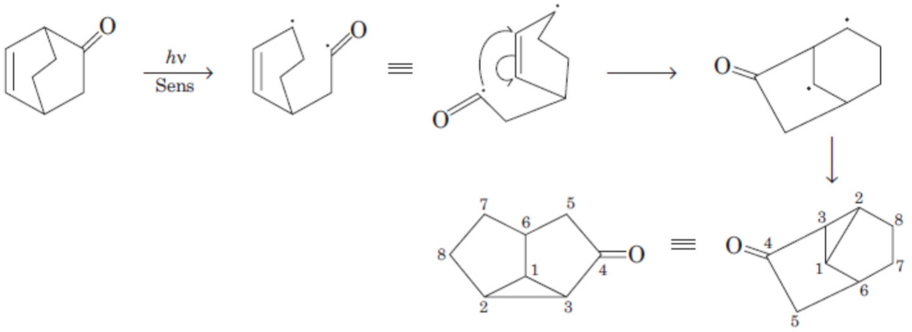
Since acyl group migrates from carbon-1 to carbon-2 of the alkenyl chain, the rearrangement due to this reason is known as 1, 2-acyl shift. 1, 2-Acyl shift given by β,γ - unsaturated ketones is known as oxa-di-π-methane rearrangement. 1, 2-acyl shift leads the formation of cyclopropane derivative.

2-Cyclopentylmethyl ketones give 1, 2-acyl shift in the presence of triplet sensitiser.



Similarly bicyclo [2, 2, 2] octenone gives 1, 3-acyl shift by direct irradiation. In the presence of triplet sensitiser it gives 1, 2-acyl shift.



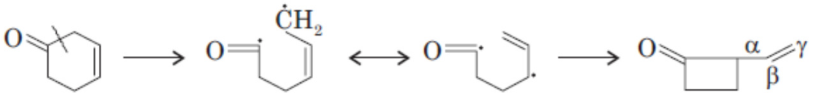


PHOTOCHEMISTRY OF NATURAL PRODUCTS HAVING β, γ-UNSATURATED KETONE GROUP

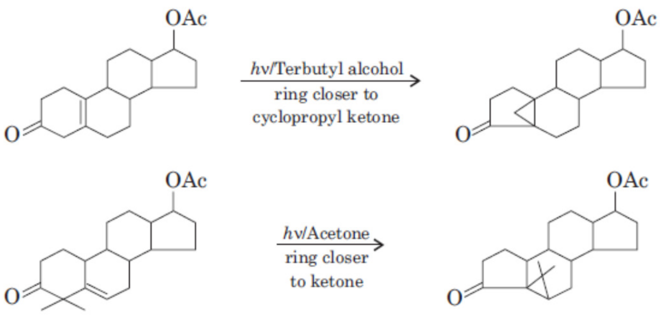
β, γ-unsaturation promotes α-cleavage of carbonyl compound because of allylic stabilisation of the radical produced.

Two modes of overall reaction are observed.

1. The first mode involves a 1, 3-acyl shift in the formation of an isomeric ®, ©-unsaturated ketones.

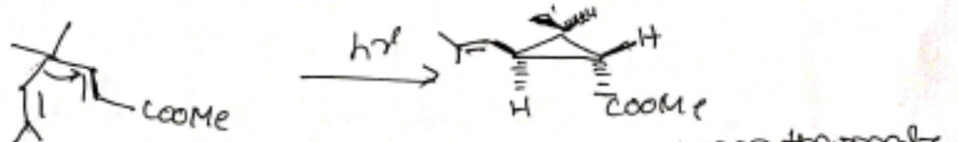


2. The second mode of reaction involves ring closure to a cyclopropyl ketone.



Applications of DPM rearrangement

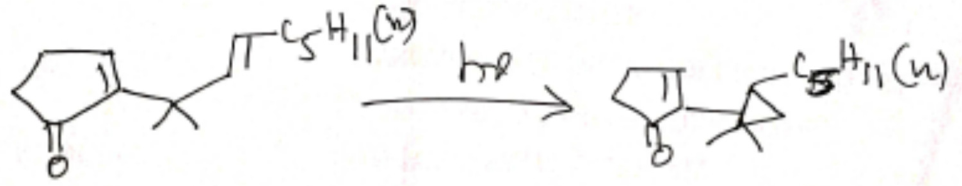
Industrial importance of DPM is in the synthesis of Methyl chrysanthemate.



Methyl chrysanthemate

The di-π-methane rearrangement is used to manufacture biodegradable insecticide that is methyl chrysanthemate.

Derivative of these compounds found in mosquito coils, goodnight etc. Slightly less used reaction in di-π-methane rearrangement is oxa-di-π-methane rearrangement, which has been used to synthesis sesquiterpenoids



Deoxy toylorine