Formation of Allenes or γ-Ketoesters from Reactions of Oxyallyls with Acetylenes or 1,1-Dimethoxyethene

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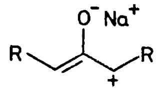
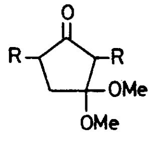
Summary Attempted formation of substituted cyclopentanones from oxyallyls and 2π-systems failed; however, novel allenic compounds (from acetylenes) or γ-ketoesters (from 1,1-dimethoxyethene) were isolated instead.

The 3 + 4 (2π + 4π) cycloadditions of oxyallyls (**1**) have been intensively studied by Noyori,[1] Hoffmann,[2] and ourselves;[3] however the 3 + 2 (2π + 2π) cycloaddition processes have received much less attention,[4,5] and the olefinic component has always lacked functional groups that could be used for further elaboration of the cycloadduct. We wished to prepare substituted cyclopentanones which possessed such functional groups, and tried the reactions of (**1**) with acetylenes and with 1,1-dimethoxyethene.

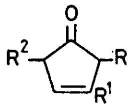
The reactions were carried out by dropwise addition of a mixture of an αα′-dibromoketone (10 mmol) (*e.g.*, 2,4-dibromopentanone) and an acetylene or 1,1-dimethoxyethene (10 mmol) in acetonitrile, to a mixture of sodium iodide (6·0 g) and copper powder (2 g) in acetonitrile, the whole being maintained at room temperature under nitrogen. Reaction was usually complete after 8—10 h, but in no instances were any of the desired cyclopentanones (**2a**) or cyclopentenones (**2b**) obtained.



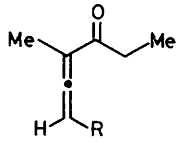
(1)



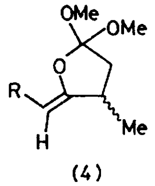
(2a)



(2b)

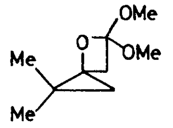


(3)



(4)

(5)



(6)

Instead, reaction between the oxyallyl species formed from 2,4-dibromopentanone, and prop-2-yn-1-ol gave the allene (**3**) ($R{=}CH_2OH$) in 25% yield† [ν_{max} 1950 and 1675 cm^{-1}; $\delta(CDCl_3)$ 5·75 (tq, 1H, *J* 3 and 6 Hz, allene H). A similar product [$R{=}CH(OEt)_2$] was obtained in 30% yield when 1,1-diethoxyprop-2-yne was employed [ν_{max} 1955 and 1685 cm^{-1}; $\delta(CDCl_3)$ 5·6 (1H, dq, *J* 3 and 6 Hz, allene H), and 1-methoxyprop-2-yne gave the product (**3**) ($R{=}CH_2OMe$) in 35% yield [ν_{max} 1952 and 1685 cm^{-1};

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† No attempt has been made to optimise the yields in these cycloadditions.

$\delta(CDCl_3)$ 5·6 (1H, tq, *J* 3 and 6 Hz, allene H). Considerable quantities of the symmetrical hexa-2,4-diynes were also produced from each of the acetylenes.

When the same oxyallyl species was allowed to react with 1,1-dimethoxyethene, the cycloadduct (**4**) (R=Me) resulted (90% yield). This was clearly distinguished from the desired product (**2a**) (R=Me) by spectroscopy [ν_{max} 3060 and 1709 cm^{-1}, enol ether; $\delta(CDCl_3)$ 1·12 (3H, d, *J* 7 Hz, CHMe), 1·56 (3H, dd, *J* 7 and 2 Hz, =CHMe), 1·6 [1H, dd, *J* 13 and 10 Hz, CHC(OMe)$_2$], 2·15 [1H, dd, *J* 13 and 8 Hz, CHC(OMe)$_2$], 2·6—3·0 (1H, m, CH$_2$C*H*Me), 3·25 (6H, 2s, separation at 100 MHz 3 Hz, OMe), and 4·2 (1H, dq, *J* 7 and 2 Hz, =CHMe)], and by its ready conversion into methyl 4-oxo-3-methylhexanoate by treatment with dilute aqueous acid or even methanol. Similar results were obtained with 2,6-dibromocyclohexanone. When 2,4-dibromoheptan-3-one was used, mixtures of both possible cycloadducts and keto-esters (after hydrolysis) were obtained, though compound (**4**) (R=Pr^n) and the corresponding keto-ester predominated (ratio *ca.* 2 : 1).

Repetition of the cycloaddition reaction using either nonacarbonyldi-iron[1] or a zinc–copper couple[2] to generate the oxyallyl species, resulted in the formation of dimers [and trimers, *i.e.* 1,3,5-trimethoxybenzene, with $Fe_2(CO)_9$] from 1,1-dimethoxyethene. No cycloadducts were obtained in any of these experiments. This provides a further illustration of the different reactivities of oxyallyls formed using copper and sodium iodide (sodium enolate), rather than nonacarbonyldi-iron or zinc–copper couples (iron or zinc enolates)[6].

In addition the formation of the cycloadduct (**4**) furnishes good evidence for the non-involvement of cyclopropanones, *e.g.* (**5**), in the reactions of oxyallyls, since it has already been shown that 2,2-dimethylcyclopropanone reacts with 1,1-dimethoxyethene to yield the cycloadduct (**6**).[7]

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