Tetrahedron Letters Vol. 21, pp 577 - 580
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0040-4039/80/0201-0577$02.00/0

ZINC CHLORIDE INDUCED CYCLOADDITION OF ALLYL CHLORIDES TO ALKYNES: A NEW CYCLOPENTENE SYNTHESIS

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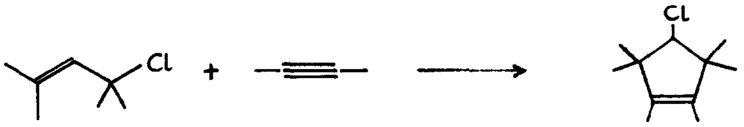
SUMMARY Zinc chloride catalyses both cycloaddition and simple addition of allylic chlorides to alkynes. The former reaction can lead to good yields of 4-chloro-cyclopentenes, and constitutes a new cyclopentene synthesis.

[4+2]-Cycloaddition (Diels Alder reaction) and [3+2]-cycloaddition (1,3-dipole reaction) processes using neutral reactants have long had an important place in the synthesis of alicyclic and heterocyclic compounds. By contrast, polar cycloadditions leading to five-membered rings, as in equation (1), were almost unknown[1] until the pioneering work of groups led by Hoffmann[2] and by Noyori.[3] Their efforts have resulted in the development of conditions favourable to [3+2]- and [3+4]-cycloaddition reactions, notably those based on oxy-allyl cations.

--- (1)

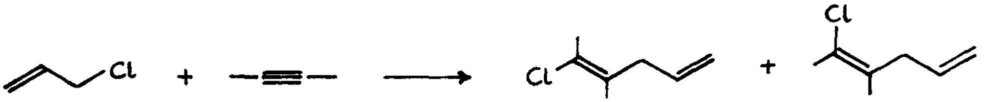
More recently, others have shown that simple Lewis acid-allyl halide interactions can produce intermediates capable of [3+4]-cycloaddition to 1,3-dienes,[4,5] or of [3+2]-cycloaddition to alkenes.[5] Our previous interest in heterogeneous Lewis acid catalysis[6] also led us to the view that such conditions might lead to cycloaddition. We now report that anhydrous zinc chloride can induce [3+2]-cycloaddition to alkynes, thus providing a new route to substituted cyclopentenes, as shown for the general case in equation (2).



--- (2)

Experimentally our procedure is extremely simple, and involves the gradual addition of an allylic chloride, **1**, to a stirred mixture of an alkyne, **2**, (1 mol. equiv.), and zinc chloride in 1,2-dichloroethane.[7] Sometimes cooling is advisable during the addition, and, after this is complete, the mixture is stirred at 20°C, for the times shown in the Table. The catalyst is then removed by filtration, and the product(s) isolated by conventional methods, usually chromatographic.

Our results (see Table) show that cycloaddition is observable with a range of allylic chlorides, **1**, and alkynes, **2**. The efficiency of cycloaddition is quite variable, and this is largely due to competition between cycloaddition (equation (2)), and simple addition (equatio (3)), to the alkyne. Cycloaddition is favoured with phenyl acetylenes, and when two possible regioisomers may be formed, only one is observed.

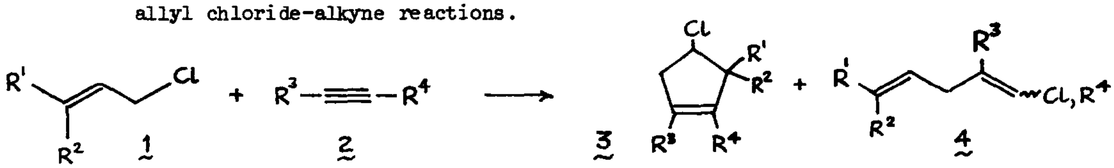


---(3)

The regiochemistry of the cycloaddition products is not uniquely established by the usual spectroscopic methods of analysis. Chemical confirmation was achieved by ozonolysis (Zn-HOAc work-up), as shown in equation (4) for the cycloadduct, **5**, of phenyl acetylene with

1-chloro-3-methylbut-2-ene. The n.m.r. of the aldehyde ozonolysis product, **6**, clearly reveals an α-β-unsaturated aldehyde structure, and allows rejection of **7** as a possible cycloaddition product.

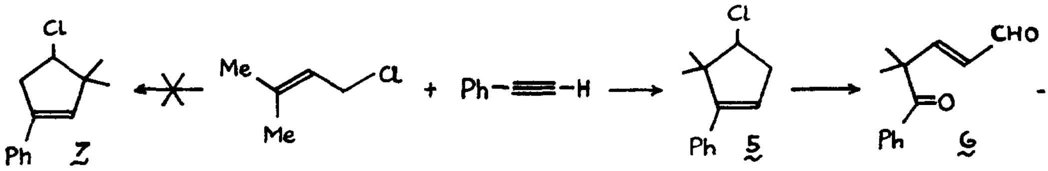
TABLE: Yields of cycloadducts[a] and of 1,4-dienes[b] from zinc chloride catalysed allyl chloride-alkyne reactions.



ALLYL CHLORIDE 1	ALKYNE 2	TIME (h)	% CYCLOADDUCT 3	% 1,3-DIENES 4
$R^1=R^2=H$	$R^3=H$, $R^4=Ph$	72	0	0
$R^1=Me$, $R^2=H$	$R^3=Me$, $R^4=Ph$	6	50	28
$R^1=Ph$, $R^2=H$	$R^3=Me$, $R^4=Ph$	3.5	33	7
$R^1=R^2=Me$	$R^3=H$, $R^4=Ph$	2	36	48
" "	$R^3=Me$, $R^4=Ph$	3	78	0
" "	$R^3={}^tBu$, $R^4=Ph$	4	57	0
" "	$R^3=R^4=Ph$	2	75	0
" "	$R^3=R^4=Et$	6	21	42
" "	$R^3=H$, $R^4={}^nBu$	12	<5	-
" "	$R^3=COOEt$, $R^4=Ph$	72	0	0

[a] appropriate microanalytical and spectroscopic data has been obtained for new structures.

[b] mixtures of cis-1-chloro- and trans-1-chloro-1,4-dienes.



--- (4)

In conclusion, this work describes the first [3+2]-cycloaddition to an alkyne,[8] and provides a one pot route to cyclopentenes not readily prepared by available methods. The synthetic prospects and mechanistic aspects of these reactions are being investigated.

References

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(Received in UK 30 November 1979)