

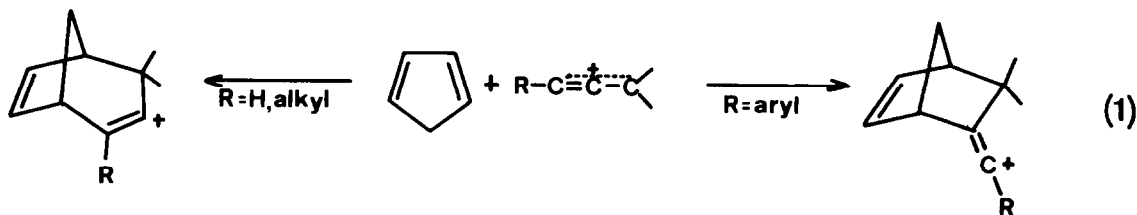
ADDITION AND CYCLOADDITION REACTIONS OF ALLENYL CATIONS WITH VARIOUS CYCLOALKA-1,3-DIENES

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Abstract: Allenyl cations $R-C^+=C(CH_3)_2$, generated *in situ* from propargyl chlorides and zinc chloride give monocyclic adducts or [3+4] and [2+4] cycloaddition products with various cycloalka-1,3-dienes. The mode of addition depends on R and the ring size of the 1,3-dienes.

Recently, we reported the formation of [3.2.1] and [2.2.1] bicyclic compounds via [3+4] and [2+4] cycloaddition reactions of allenyl cations with cyclopentadiene (eq 1).^{1,2}

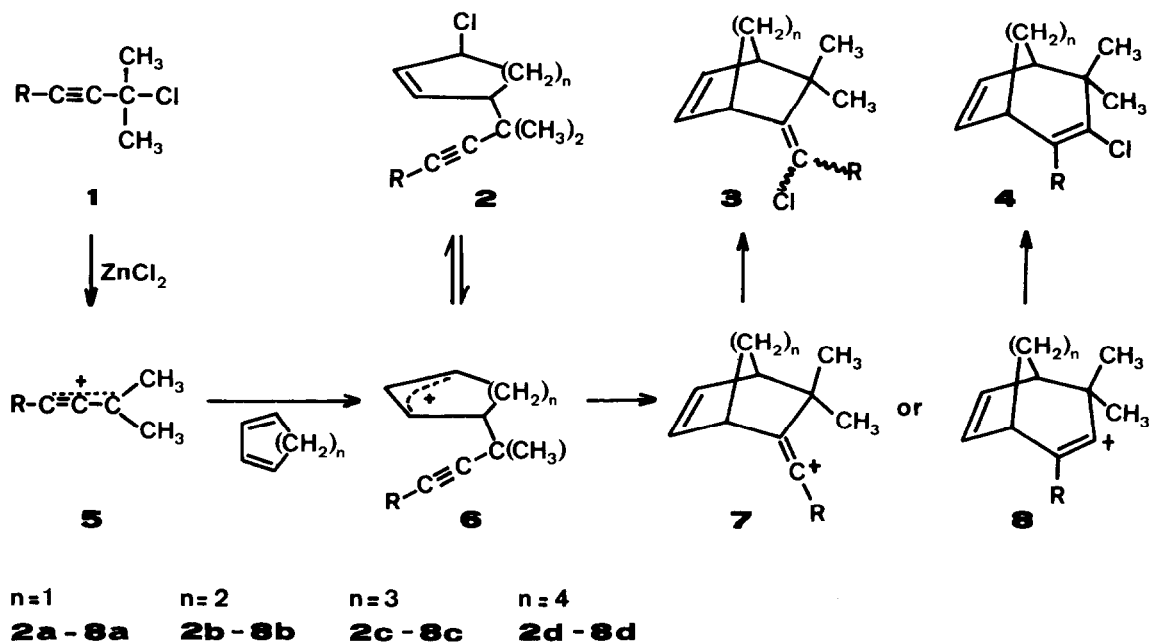


We have now investigated the corresponding addition reactions of allenyl cations to higher cyclic 1,3-dienes. As described previously,² the reactions were carried out by adding approximately equimolar mixtures of dienes and propargyl chlorides 1 to solutions of zinc chloride - ether in dichloromethane at low temperatures.

As shown in Table 1, [3+4]cycloaddition reactions yielding vinyl chlorides 4, can only be observed when allenyl cations 1 (R = alkyl) are combined with cyclopentadiene.² Cyclohexadiene and cycloheptadiene afford [2+4]cycloaddition products 3 exclusively; for R=CH₃, 1:1 mixtures of (*E*)- and (*Z*)-isomers are obtained, while for R=Ph only (*E*)-vinyl chlorides 3 can be detected. Cyclooctadiene reacts more slowly than the other dienes yielding 3-alkynyl-8-chloro-cyclooctenes 2d (mixture of isomers). Treatment of allyl chlorides 2d with zinc chloride at 0°C does not yield bicyclic compounds but results in HCl-elimination affording 5-alkynyl-1,3-cyclooctadienes.

Norbornenes 3b-Ph and 3c-Ph are identified by spectral comparison with the previously assigned homolog 3a-Ph.² The corresponding methyl compounds 3b-CH₃ and 3c-CH₃ show ¹H-NMR resonances at δ 2.10-2.23, in accord with the structural element =C(CH₃)Cl; for the 4-CH₃ isomers absorptions at higher field are expected, as observed for 4a-CH₃ (δ 1.82).² Conclusive struc-

tural evidence comes from catalytic (Pd/C) hydrogenation of $\underline{3b}$ -CH₃, yielding 2-(α -chloroethylidene)-3,3-dimethyl-bicyclo [2.2.2] octane, which affords 3,3-dimethylbicyclo [2.2.2] octan-2-one³ on ozonolysis.



Compounds $\underline{2}$ - $\underline{4}$ are derived from cations $\underline{6}$ - $\underline{8}$, respectively. In order to rationalise the different addition products obtained from various dienes, we estimated the relative energies of carbenium ions $\underline{6}$ - $\underline{8}$ (Table 2). Force field calculations⁴ provide heats of formation of hydrocarbons $\underline{9}$ - $\underline{11}$, which are assumed to reflect the relative energies of $\underline{2}$ - $\underline{4}$, respectively. Solvolysis rates of model compounds are used to estimate the energy difference between $\underline{2}$ - $\underline{4}$ and the corresponding carbenium ions $\underline{6}$ - $\underline{8}$ (Table 2, Fig. 1).

Table 1: Products of ZnCl₂ Catalysed Reactions of Propargyl Chlorides $\underline{1}$ with Cycloalka-1,3-dienes^a

n	R	Conditions ^b	Product ^c	Yield ^d	mp.(°C)/bp.(°C,Torr)
1	CH ₃	3h, -30°C	$\underline{4a}$ -CH ₃	36%	37/0.05
1	Ph	0.5h, -50°C	(<i>E</i>)- $\underline{3a}$ -Ph	65%	79-80
2	CH ₃	4h, -30°C	(<i>E</i>), (<i>Z</i>)- $\underline{3b}$ -CH ₃	22%	65-70/0.03 ^e
2	Ph	0.5h, -50°C	(<i>E</i>)- $\underline{3b}$ -Ph	54%	67-68.5
3	CH ₃	7h, -30°C	(<i>E</i>), (<i>Z</i>)- $\underline{3c}$ -CH ₃	22%	80-85/0.05 ^e
3	Ph	2h, -40°C	(<i>E</i>)- $\underline{3c}$ -Ph	50%	43-44
4	CH ₃	f	$\underline{2d}$ -CH ₃	10%	90-95/0.1
4	Ph	14d, -78°C	$\underline{2d}$ -Ph	29% ^g	h

^a Reaction products confirmed by ¹H-, ¹³C-NMR, IR, MS and CH analyses; ^b Catalyst concentration see ref. 2; ^c Lacking material is polymeric; ^d Isolated yield of pure material; ^e Bath temperature; ^f 12d -78°C, warmed up to -45°C within 12h; ^g In one experiment 1% of an impure

product, probably $\underline{3d}$ -Ph was isolated in addition;^h Oil, purified by column chromatography.

As discussed previously,^{1,2} propargyl halides $\underline{1}$ dissociate in the presence of ZnCl_2 giving allenyl cations $\underline{5}$. Attack of 1,3-dienes at the sp^2 carbon of $\underline{5}$ affords cycloalkenyl cations $\underline{6}$, which either combine with chloride ions to give $\underline{2}$ or undergo π -cyclisation yielding $\underline{7}$ and $\underline{8}$.

Table 2 shows that the cyclopentadiene addition product $\underline{4a}$ ($\cong \underline{11a}$) is 9 kcal/mol more stable than $\underline{3a}$ ($\cong \underline{10a}$). This energy difference is responsible for the higher stability of $\underline{8a}$ - CH_3 relative to $\underline{7a}$ - CH_3 , even though the vinyl cation fragment in $\underline{8}$ cannot achieve the ideal linear geometry.⁵ A phenyl group, however, stabilises $\underline{7}$ so effectively that the higher strain in the [2.2.1]bicyclic system is overcompensated, and $\underline{7a}$ -Ph is more stable than $\underline{8a}$ -Ph: allenyl cations with $\text{R}=\text{Ph}$ and $\text{R}=\text{CH}_3$ undergo different types of cycloaddition with cyclopentadiene (Fig. 1a).²

On the other hand, vinyl chlorides $\underline{3b}$, \underline{c} ($\cong \underline{10a,b}$) and $\underline{4b}$, \underline{c} ($\cong \underline{11b,c}$) are similar in energy (Table 2). Therefore, carbenium ions $\underline{7b}$, \underline{c} with the linear vinyl cation fragment are more stable than the endocyclic vinyl cations $\underline{8b}$, \underline{c} ,⁶ independent of the nature of R: both cyclohexadiene and cycloheptadiene undergo [2+4] cycloadditions exclusively (Fig. 1b).

If allyl halides $\underline{2a-c}$ are formed as intermediates, they will redissociate and successively yield vinyl cations $\underline{7}$ and $\underline{8}$, which are irreversibly trapped by chloride ions.⁷ According to Table 2, $\underline{2d}$ dissociates very slowly (ΔG^\ddagger); a high activation barrier for the rearrangement of $\underline{2d}$ to $\underline{3d}$ via $\underline{6d}$ results, rationalising the formation of monocyclic products $\underline{2d}$ from $\underline{1}$ and cyclooctadiene.

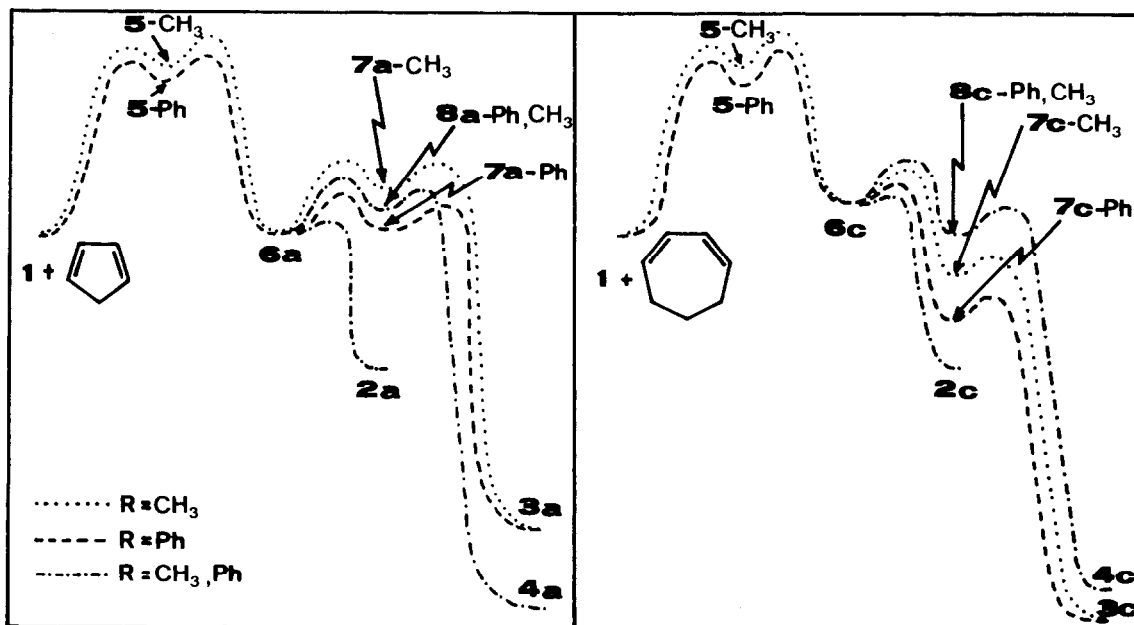
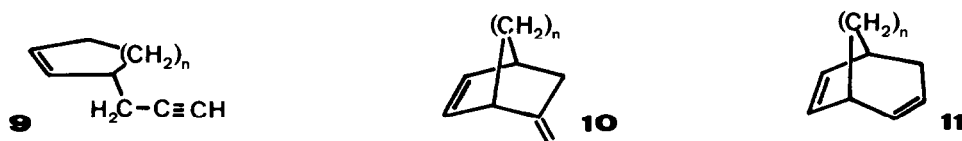


Fig. 1: Schematic energy diagrams for the Lewis acid catalysed additions of propargyl chlorides $\underline{1}$ to cyclopentadiene (a) and cycloheptadiene (b).

Table 2: Computation of Relative Energies (kcal/mol) of Carbenium Ions $\underline{6}$ - $\underline{8}$ ^a

n	ΔH_f°	ΔG^\ddagger	rel.E	ΔH_f°	ΔG^\ddagger	rel.E	ΔG^\ddagger	rel.E	ΔH_f°	ΔG^\ddagger	rel.E
	($\underline{9}$) ^b	c,d	($\underline{6}$)	($\underline{10}$) ^b	c,e	($\underline{7-CH_3}$)	c,f	($\underline{7-Ph}$)	($\underline{11}$) ^b	c	($\underline{8}$)
1	60.7	16.1	0.0	41.5	41.1	5.8	35.8	0.5	32.5	47.4 ^g	3.1
2	51.8	20.0	0.0	28.3	41.1	-2.4	35.8	-7.7	29.3	42.3 ^h	-0.2
3	51.7	19.7	0.0	21.8	41.1	-8.5	35.8	-13.8	25.4	42.3 ^h	-3.7
4	48.0	22.6	0.0	16.9	41.1	-12.6	35.8	-17.9	24.5	42.3 ^h	-3.8

^a See text for procedure; ^b ΔH_f° calculated with Allinger's force field MM1 (ref. 4); ^c ΔG^\ddagger corresponds to solvolysis reactions of allyl and vinyl bromides in 80% EtOH; a correction factor $k_{OTf}/k_{Br} = 6 \cdot 10^7$ was applied, if solvolysis constants of triflates were used: ref. 8; ^d ΔG^\ddagger (25°C) of 3-bromocycloalkenes: ref. 9; ^e ΔG^\ddagger (100°C) of $(CH_3)_2C=C(OTf)CH_3$ ($\underline{12}$): ref. 10; ^f ΔG^\ddagger (120°C) of $(CH_3)_3C=C(Br)-Ph$: ref. 11; ^g From relative solvolysis rates of 1-cyclohexenyl triflate (ref. 5) and $\underline{12}$; ^h From relative solvolysis rates of 1-cycloheptenyl triflate (ref. 5) and $\underline{12}$.

References and Notes

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