Tetrahedron Letters Vol. 22, pp 925 - 928
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0040-4039/81/0301-0925$02.00/0

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

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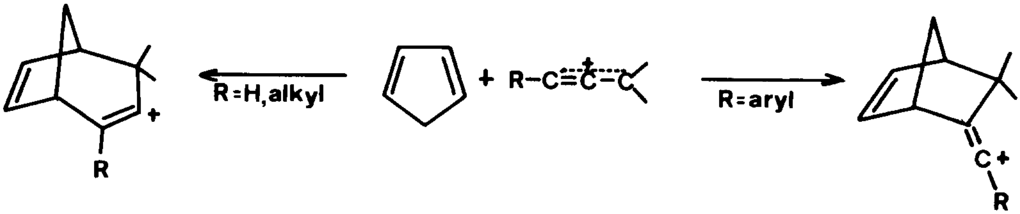
Abstract: Allenyl cations $R\text{-}C\equiv\overset{+}{C}\text{-}C(CH_3)_2$, generated in situ from propargyl chlorides and zinc chloride give monocyclic adducts or [3+4] and [2+4] cycloaddition products with various cycloalka-1,3-dienes. The mode of addition depends on R and the ring size of the 1,3-dienes.

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]

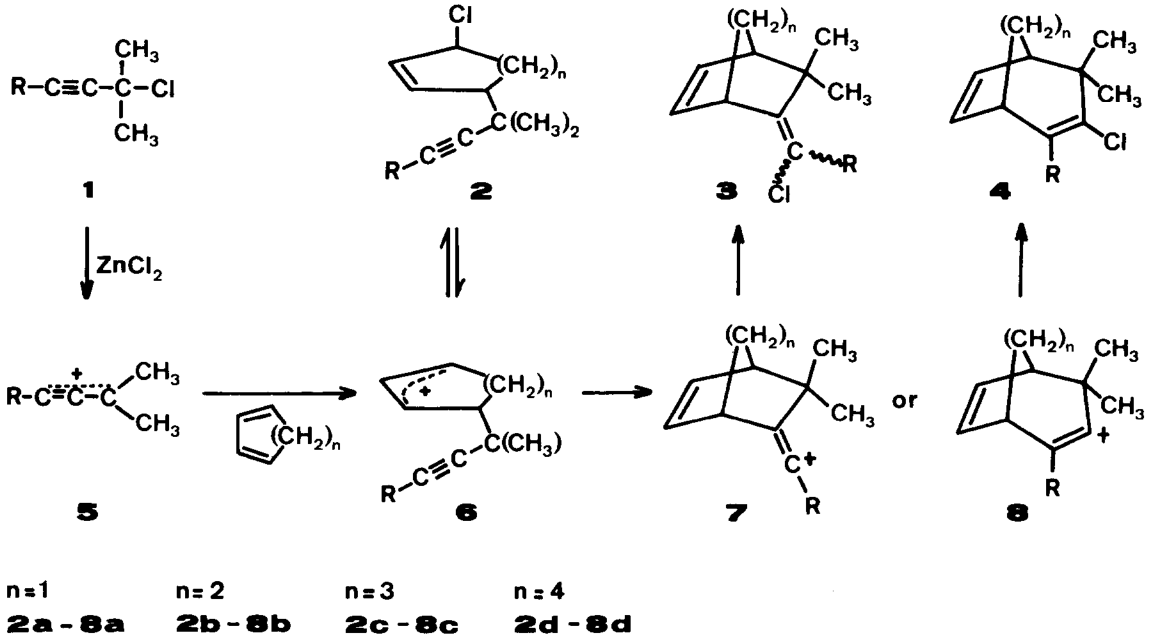


(1)

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=CH_3, 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-CH_3 and 3c-CH_3 show ^{1}H-NMR resonances at δ 2.10-2.23, in accord with the structural element =$C(CH_3)Cl$; for the 4-CH_3 isomers absorptions at higher field are expected, as observed for 4a-CH_3 (δ 1.82).[2] Conclusive structural evidence comes from catalytic (Pd/C) hydrogenation of 3b-CH_3, yielding 2-(α-chloroethylidene)-3,3-dimethyl-bicyclo [2.2.2] octane, which affords 3,3-dimethylbicyclo [2.2.2] octan-2-one[3] on ozonolysis.



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

Table 1: Products of $ZnCl_2$ Catalysed Reactions of Propargyl Chlorides 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	4a-CH_3	36%	37/0.05
1	Ph	0.5h, -50°C	(E)-3a-Ph	65%	79-80
2	CH_3	4h, -30°C	(E),(Z)-3b-CH_3	22%	65-70/0.03[e]
2	Ph	0.5h, -50°C	(E)-3b-Ph	54%	67-68.5
3	CH_3	7h, -30°C	(E),(Z)-3c-CH_3	22%	80-85/0.05[e]
3	Ph	2h, -40°C	(E)-3c-Ph	50%	43-44
4	CH_3	[f]	2d-CH_3	10%	90-95/0.1
4	Ph	14d, -78°C	2d-Ph	29%[g]	[h]

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[a] Reaction products confirmed by ^{1}H-, ^{13}C-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 **3d**-Ph was isolated in addition; [h] Oil, purified by column chromatography.

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

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

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

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

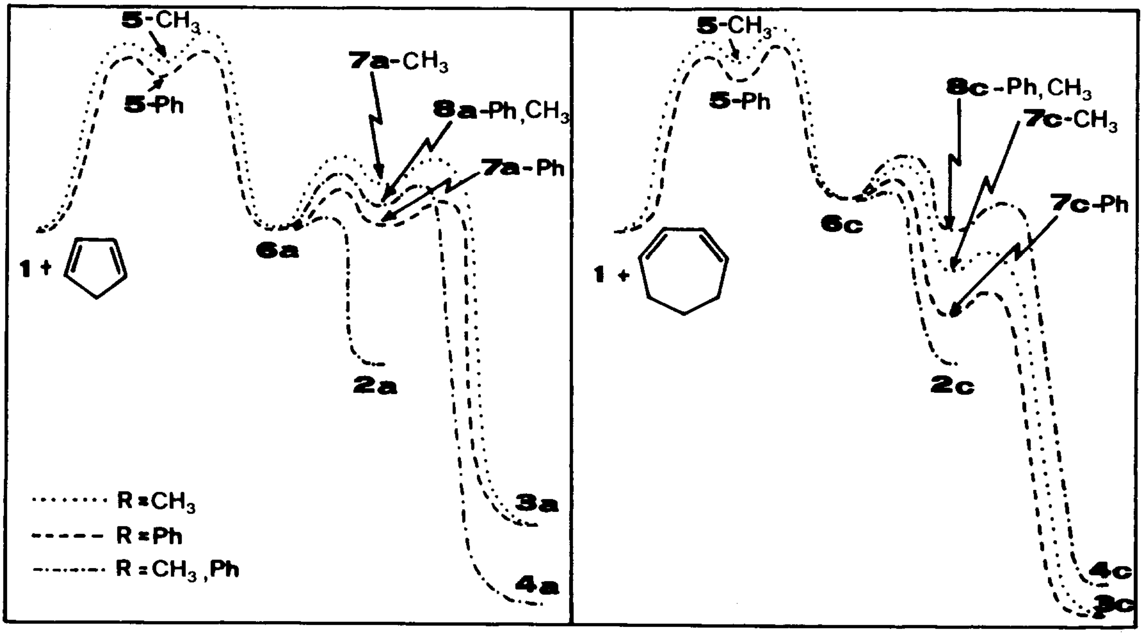
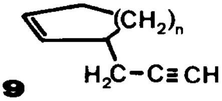


Fig. 1: Schematic energy diagrams for the Lewis acid catalysed additions of propargyl chlorides **1** to cyclopentadiene (a) and cycloheptadiene (b).

Table 2: Computation of Relative Energies (kcal/mol) of Carbenium Ions 6-8[a]



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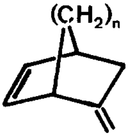

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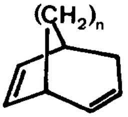

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	n	ΔH_f^o (9)[b]	$\Delta G^\ddagger$ c,d	rel.E (6)	ΔH_f^o (10)[b]	$\Delta G^\ddagger$ c,e	rel.E (7-CH_3)	$\Delta G^\ddagger$ c,f	rel.E (7-Ph)	ΔH_f^o (11)[b]	$\Delta G^\ddagger$ c	rel.E (8)
a	1	60.7	16.1	0.0	41.5	41.1	5.8	35.8	0.5	32.5	47.4[g]	3.1
b	2	51.8	20.0	0.0	28.3	41.1	-2.4	35.8	-7.7	29.3	42.3[h]	-0.2
c	3	51.7	19.7	0.0	21.8	41.1	-8.5	35.8	-13.8	25.4	42.3[h]	-3.7
d	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^o calculated with Allinger's force field MM1 (ref. 4); [c] $\Delta G^\ddagger$ 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] $\Delta G^\ddagger$ (25°C) of 3-bromocycloalkenes: ref. 9; [e] $\Delta G^\ddagger$ (100°C) of $(CH_3)_2C{=}C(OTf)CH_3$ (12): ref. 10; [f] $\Delta G^\ddagger$ (120°C) of $(CH_3)_3C{=}C(Br){-}Ph$: ref. 11; [g] From relative solvolysis rates of 1-cyclohexenyl triflate (ref. 5) and 12; [h] From relative solvolysis rates of 1-cycloheptenyl triflate (ref. 5) and 12.

References and Notes

(1) H. Mayr and B. Grubmüller, Angew. Chem., **90**, 129 (1978); Angew. Chem. Int. Ed. Engl., **17**, 130 (1978).

(2) H. Mayr and I. K. Halberstadt, Angew. Chem., **92**, 840 (1980); Angew. Chem. Int. Ed. Engl., **19**, 814 (1980).

(3) J. B. Stothers and C. T. Tan, Can. J. Chem., **54**, 917 (1976).

(4) N. L. Allinger, Adv. Phys. Org. Chem., **13**, 1 (1976); QCPE Program No. 318.

(5) W. D. Pfeiffer, C. A. Bahn, P. v. R. Schleyer, S. Bocher, C. E. Harding, K. Hummel, M. Hanack, and P. J. Stang, J. Am. Chem. Soc., **93**, 1513 (1971).

(6) See also: L. G. Kozar, R. D. Clark, and C. H. Heathcock, J. Org. Chem., **42**, 1386 (1977).

(7) 2a-H instantaneously rearranges to 4a-H under reaction conditions: H. Mayr, Habilitationsschrift, Erlangen, 1980.

(8) k_{OTf}/k_{Br} obtained from data in C. A. Grob and G. Cseh, Helv. Chim. Acta, **47**, 194 (1964) and P. J. Stang, R. J. Hargrove, and T. E. Dueber, J. C. S. Perkin Trans. 2, **1977**, 1486.

(9) P. v. R. Schleyer and W. F. Sliwinski, unpublished results.

(10) R. H. Summerville, C. A. Senkler, P. v. R. Schleyer, T. E. Dueber, and P. Stang, J. Am. Chem. Soc., **96**, 1100 (1974).

(11) J.-L. Derocque, F.-B. Sundermann, N. Youssif, and M. Hanack, Liebigs Ann. Chem., **1973**, 419.

This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. We thank Professor P. v. R. Schleyer for communicating solvolysis data of cycloalkenyl bromides to us prior to publication.

(Received in Germany 11 December 1980)