Tetrahedron Letters,Vol.27,No.46,pp 5653-5656,1986 0040-4039/86 $3.00 + .00
Printed in Great Britain Pergamon Journals Ltd.

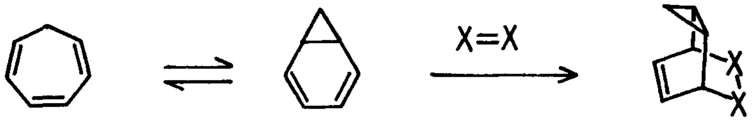
POSITION AND DIENOPHILE DEPENDENT DIELS-ALDER REACTIONS OF VINYLCYCLOHEPTATRIENES

Michihiro Aga, Keiji Okada, and Masaji Oda*
Department of Chemistry, Faculty of Science, Osaka University,
Toyonaka, Osaka 560, Japan

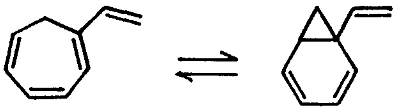
Summary: While 1-vinyl- and 2-vinylcycloheptatrienes undergo Diels-Alder reactions exclusively from cycloheptatriene forms at the diene part including the vinyl group, 3-vinylcycloheptatriene reacts site-selectively from either cycloheptatriene or norcaradiene form depending on electron affinity of dienophiles.

Diels-Alder reactions of cycloheptatriene (1A, CHT) proceed almost exclusively through the norcaradiene form (1B, NCD).[1)] Although the origin of this high chemoselectivity has not been well understood, decreased reactivity of CHT-form due to boat conformation (a steric effect) may be one of the major reasons. Introduction of a vinyl group on CHT may affect the reactivity and selectivity of the CHT⇌NCD system by altering the steric and electronic effects. For 1-, 2-, and 3-vinylcycloheptatrienes and their NCD-forms (2A⇌2B, 3A⇌3B, and 4A⇌4B), there are four (for 2) or five possible sites (for 3 and 4) for Diels-Alder reactions.

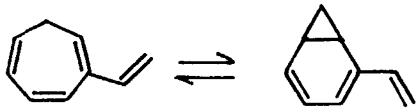
We previously reported that 4π electrocyclization of cycloheptatrienyldiphenylmethyl cations(5)are sharply dependent on the substitution-position on CHT: while 1- and 2-isomers cyclize only from the CHT-forms, 3-isomer cyclizes only from the NCD-form.[2)] Here, we have examined Diels-Alder reactions of 2~4 to see the dependency of chemoselectivity and site-selectivity on substitution-position and dienophile-reactivity.



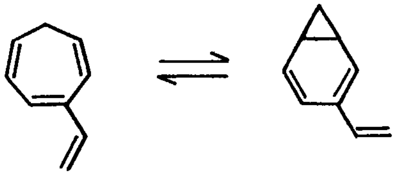
1A 1B



2A 2B



3A 3B



4A 4B

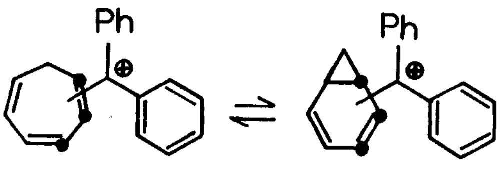


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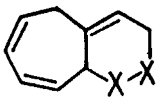
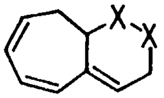
Table 1. Diels-Alder reactions of vinylcycloheptatrienes

Compound	Dienophile[a]	Solvent	Temperature °C	Product (mp °C)	Yield[b] %
1-Vinyl- 2	NPTAD	CH_2Cl_2	-70	6a (156)	97
	TCNE	CH_2Cl_2	20	6b (100)	80
	DCA	$CDCl_3$	37	6c (74)	96
	DMAD	Toluene	70	6d (oil)	82
2-Vinyl- 3	NPTAD	CH_2Cl_2	-70	7a (183)	60
	TCNE	CH_2Cl_2	20	7b (105)	70
	DCA	$CDCl_3$	37	7c (97)	84
	DMAD	Toluene	70	7d (oil)	88
3-Vinyl- 4	NPTAD	CH_2Cl_2	-70	8a (163)	95
	TCNE	CH_2Cl_2	20	8b (153)	75
	DCA	$CDCl_3$	37	9c (98)	68
	DMAD	Toluene	110	9d (oil)	98
	FMN	Toluene	120[c]	9e (109)	71
	NQ	Toluene	120[c]	9f (125)	56

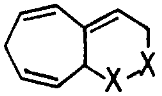
[a] 1.1-1.2 Equiv. were used except for NQ (2.0 equiv.), and see the text for the abbreviations. [b] Isolated yield. [c] In an ampoule.



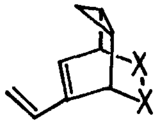
6a~d



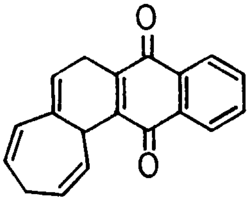
7a~d



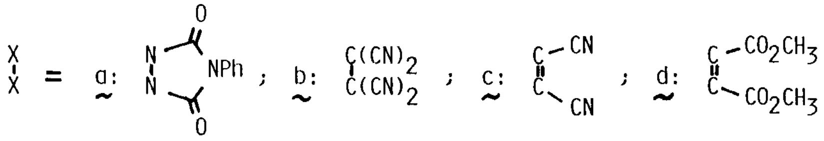
9c~e



8a, b



9f



Vinylcycloheptatrienes (2, 3, and 4)[3,4] were selectively prepared by the reaction of 1-,[5] 2-,[6] and 3-formylcycloheptatriene[7] with methylenetriphenylphosphorane. The NMR spectra of 2~4 at ambient temperature are in accord with the CHT structures and show no sign of equilibrium with the NCD-forms.[3] As dienophiles, principally following four compounds were employed by taking account of symmetry (for simplification of the structural analyses of the adducts) and range of reactivity (for seeing dienophile-dependency and selectivities): N-phenyltriazolinedione (NPTAD), tetracyanoethylene (TCNE), dicyanoacetylene (DCA), and dimethyl acetylenedicarboxylate (DMAD).

The results of the Diels-Alder reactions are summarized in Table 1.[8] Both 1- and 2-vinylcycloheptatrienes (2 and 3) give the adducts (6a~d and 7a~d, respectively) from the CHT-forms chemoselectively and site-selectively. Thus, the diene part including the vinyl group in the CHT-forms of 2 and 3 is most reactive or at least reactive enough for preventing detectable competition from the NCD-forms (2B and 3B). On the other hand, 3-vinyl isomer (4) shows a remarkable dienophile-dependency: while DCA and DMAD afford selectively the CHT-adducts (9c and 9d, respectively) similar to the reactions with 2 and 3, NPTAD and TCNE do only the NCD-adducts (8a and 8b, respectively) site-selectively. Other dienophiles such as fumaronitrile (FMN) and 1,4-naphthoquinone (NQ) behave similarly with DCA and DMAD yielding 9e and 9f, respectively. The adduct (9f) is a secondary product formed by dehydrogenation of the initial Diels-Alder adduct with existing NQ.

The rate constants of the reactions of 1~4 with DCA (Table 2) show much higher reactivity of 2~4 than cycloheptatriene itself (1). It is notable that the 3-vinyl isomer (4) which shows the dienophile-dependency is considerably less reactive than 2 and 3. The enhanced reactivity of 2~4 over 1 may be ascribed to feasibility of the reacting diene part to take coplanar conformation as well as to higher HOMO energy owing to longer conjugation.

Table 2. Kinetics of Diels-Alder reactions of vinylcycloheptatrienes with dicyanoacetylene.[a]

Compound	$10^3 \cdot k$ (l/mol·sec)
Cycloheptatriene 1	0.15 (80 °C)
1-Vinyl- 2	1.55 (37 °C)
2-Vinyl- 3	1.35 (37 °C)
3-Vinyl- 4	0.40 (37 °C)

[a] Measured by ^{1}H NMR spectroscopy in $CDCl_3$ using 1,4-di-t-butylbenzene as an internal standard.

The general reactivity sequence of the employed dienophiles for Diels-Alder reactions with normal electron demand is NPTAD > TCNE > DCA > FMN, DMAD, NQ.[9] Qualitative reactivity of these dienophiles toward 2~4 agrees with this reactivity sequence (see the reaction conditions in Table 1). It is well known that dienophilic reactivity of electron poor olefins in electronically controled Diels-Alder reactions correlates with their LUMO energies or electron affinity (EA).[10] TCNE has a very high EA (2.88 eV; cf. 0.78 eV of FMN and -1.3 eV of ethylene).[10b] The EA of NPTAD is not known, but its strong dienophilic property speaks a high EA. Thus, in the reaction of 4, powerful dienophiles with high EA (NPTAD and TCNE) favor addition at the cyclic diene part of the NCD-form (4B) rather than addition to the CHT-form (4A), which suggests responsibility of an electronic effect for the change of chemoselectivity and site-selectivity.

Although further studies are necessary for conclusion, we think that the decreased reactivity of **4A** compared to **2A** and **3A** makes electronic effects relatively more important for the selectvivities and allows, in the reactions with strong dienophiles, the transition state from **4B** leading to **8** to become energetically most favorable probably owing to charge transfer stabilization.

References and Notes

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4) ^{13}C NMR (CDCl$_3$): **2**, δ = 26.98, 114.04, 122.73, 126.09, 127.31, 130.45, 130.70, 132.08, 138.04; **3**, δ = 27.57, 112.74, 123.33 (overlapped), 126.96, 128.15, 131.54, 136.36, 137.73; **4**, δ = 27.90, 113.55, 122.06, 122.81, 124.17, 126.77, 130.99, 140.00; UV (cyclohexane), λ_{max} (log ε): **2**, 222.5 (3.42), 228.5 (3.38), 300 nm (2.91); **3**, 229 (3.41), 237 (sh, 3.30), 265 nm (sh, 2.55); **4**, 230 (3.21), 237 (sh, 3.08), 282.5 nm (3.03).
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6) This aldehyde was obtained in 73% yield in more than 95% isomeric purity by photochemical isomerization of 1-formylcycloheptatriene5) in benzene (high pressure Hg lamp, Pyrex filter, 3 h). ^{1}H NMR (CDCl$_3$), δ = 2.50 (2H, t, J = 6.8 Hz), 5.37 (1H, dt, 9.0, 6.8 Hz), 6.13 (2H, m), 6.63 (1H, dd, 11.2, 5.2 Hz), 7.00 (1H, d, 11.2 Hz), 9.40 (1H, s); For other preparation of this compound and 3-formyl isomer, see; G. Buchi and E.M. Burgess, J. Am. Chem. Soc., 84, 3104 (1962).
7) This aldehyde was prepared by oxidation (COCl$_2$-DMSO-NEt$_3$11)) of 3-hydroxymethylcycloheptatriene12). ^{1}H NMR (CDCl$_3$), $\delta \doteq$ 2.38 (2H, t, J = 6.8 Hz), 5.6 (2H, m), 6.42 (1H, dd, 9.4, 6.0 Hz), 6.63 (1H, d, 9.4 Hz), 7.23 (1H, d, 6.0 Hz), 9.56 (1H, s).
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(Received in Japan 29 July 1986)