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NORCARADIENE - CYCLOHEPTATRIENE EQUILIBRIUM IN 7-ALKYL-7-CYANOCYCLOHEPTATRIENES

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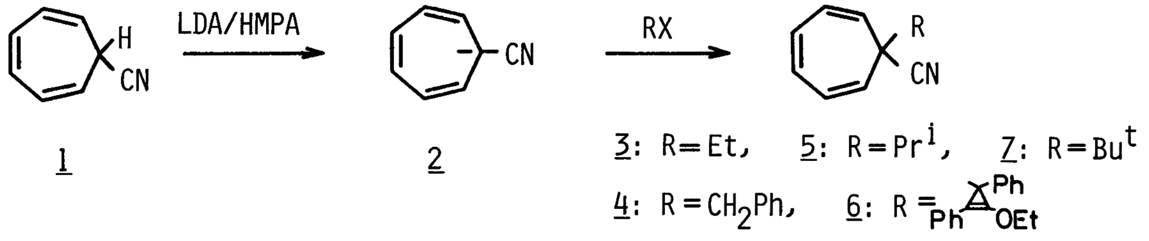
The steric effect on the cycloheptatriene (CHT) - norcaradiene (NCD) equilibrium has been studied in simple 7-alkyl-7-cyanocycloheptatrienes, such as 7-ethyl-, 7-benzyl-, 7-isopropyl-, 7-cyclopropenyl-, and 7-tert-butyl-7-cyanocycloheptatrienes. The NCD component increases with bulkiness of the 7-alkyl group in this order, but the cycloheptatriene carrying an extremely bulky 7-tert-butyl group is out of this order.

There have appeared a lot of experimental and theoretical studies on the mechanism of the symmetry-allowed valence isomerization of cycloheptatriene (CHT) and norcaradiene (NCD) systems,[1-5] and some important factors contributing to the isomerization equilibrium have been proposed, e.g. a) the stabilizing interaction due to the mixing of the acceptor orbital of the electron attracting C-7 substituent into the antisymmetric component of the Walsh orbital pair at C-1,6,[6,7] b) the substitution sites on the cycloheptatriene ring,[2,8,9,10] c) the external angle at C-7 position,[11,12] and d) the non-bonding interaction between a C-3,4 π-bond and an axial C-7 substituent.[13] We now propose another responsible factor to force the equilibrium to the side of NCD, that is the non-bonding interaction between a C-7 equatorial substituent and H-1,6 atoms in the cycloheptatriene form.

To a solution of carbanion 2[14] in THF prepared by treating 1 with LDA in the presence of HMPA, were added excess alkyl halides such as ethyl iodide, benzyl bromide, isopropyl iodide, and tert-butyl bromide at room temperature to give 7-alkyl-7-cyanocycloheptatrienes 3, 4, 5, and 7, respectively. Treatment of an acetonitrile solution of 1 with 1-ethoxy-2,3-diphenylcyclopropenium ion and diiso-



1

2

3: R=Et, 5: R=Pr^i, 7: R=Bu^t

4: R=CH$_2$Ph, 6: R=

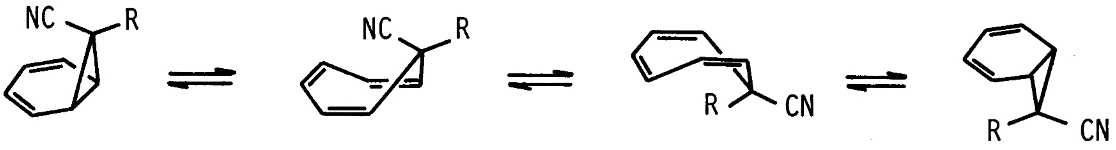
propylamine gave cyclopropenyl derivative 6 (Table 1).

The NMR spectral H-1 (H-6) chemical shifts and coupling constants J1,2 (J5,6) of 3, 4, 5, and 7 are intermediate between those of 7-cyanocycloheptatriene (1)[15] and 7,7-dicyanonorcaradiene (8),[2a,b] indicating that compounds 3, 4, 5, and 7 are in rapid equilibrium between the CHT and NCD valence isomers at room temperature (Table 1).[16] The H-1,6 chemical shift of 6 (Table 1) suggests that the NCD isomer is a major component at room temperature.[17] The H-1,6 chemical shifts of these compounds are temperature dependent and, on cooling below -130 °C, those of 5 and 7 split up into two new signals (Table 2). The H-1,6 signal of 6 shifts to upfield on cooling and becomes insensitive to temperature below -80 °C converging to almost 100% NCD proportion, while those of 3 and 4 shift to downfield on cooling, indicating an increased CHT proportion. The proportion of the NCD isomers at each temperature, enthalpy- ($\Delta H°$) and entropy- ($\Delta S°$) differences for the conversion of the NCD to the CHT are listed in Table 2. It was thus clarified that the relative proportion of the NCD component increases with the bulkiness of the alkyl substituent at C-7 position in the order of 3<4<5<<6. Due to the first sort of non-bonding interaction between an axial C-7 alkyl substituent and

Table 1. Physical and Spectral Data of 7-Alkyl-7-cyanocycloheptatrienes

Compd.	Bp or mp °C	Yield %	MS m/e (%)	UV λmax nm (ε)	^{1}H NMR (CDCl$_3$) δ1,6(ppm)	J1,2(Hz)
3	55-56 /1.5 mmHg	47	145(23), 117(62) 116(100), 91(46)	259 (4270)	4.84	8.0
4	78-79 /3.5 mmHg	36	207(7), 129(36) 117(10), 116(100)	258 (3640)	4.66	8.0
5	65-66 /0.8 mmHg	62	159(10), 144(14) 117(100), 116(80)	259 (3320)	4.36	7.0
6	pasty oil	21	351(45), 322(46) 244(59), 216(100)	267 (2400)	3.04	3.0
7	90-91	9	173(14), 131(35) 117(100), 116(20)	260 (2620)	4.69	8.0
1[2a]				255 (3710)	5.37	9.0
8[2a]				271 (2920)	3.47	5.87

a C-3,4 π-bond, the C-7 alkyl substituent is believed to be at an equatorial site, hence the population of the isomers C and D would be very low especially in



A B C D

the cases of 5 anf 6, but they (5 and 6) nevertheless exist in a higher population of the NCD component than 3 and 4. Therefore, we must make much of the second sort of non-bonding interaction between an equatorial C-7 alkyl substituent and H-1,6 atoms[18] in the A-type NCD and B-type CHT isomers, which would be less in the former than in the latter. The steric repulsion between an equatorial C-7 alkyl substituent and H-1,6 atoms pushes the C-7 atom away from the plane determined by the C-1,2,5, and 6, thereby twists away the C-1,6 π-orbitals from the parallelism of the C-2,5 π-orbitals, favoring the A-type NCD over B-type CHT structure. This explanation would be applicable to the cycloheptatrienes carrying one or more bulky substituents not only at C-7 position but also at C-1,6 and/or at C-2,5 positions, because such substituents also tend to twist the π-orbitals of C-1,6 out of those of C-2,5 due to the steric repulsion by the neighboring hydrogen atoms.

According to the above rationalization, compound 7 carrying an extremely bulky 7-tert-butyl group would exist in the A-type NCD isomer in a higher population than 5 or 6, because the second sort of non-bonding interaction in 7 seems to be much more serious than those in 5 and 6.[19] Contrary to expectation, the

Table 2. Temperature Dependence of the H-1,6 Chemical Shifts δ(ppm), Proportion of the NCD Isomers (%), Enthalpy and Entropy Differences of NCD - CHT.

T °C Compd.	34	-50	-80	-90	-100	-110	a: NCD b: CHT	$\Delta H°$	$\Delta S°$
3	4.84 (12.6)	4.86 (11.8)	4.89 (10.8)	5.07 (4.5)	5.21 (0)	5.20 (0)	*		
4	4.66 (19)	4.70 (17.5)	4.76 (15.4)	4.96 (8.4)	5.04 (5.6)	5.16 (1.4)	*		
5	4.36 (24.6)	4.32 (26)	4.31 (26.5)	——	4.28 (27.6)	coalesce	a:2.34** b:5.02 (-130°C)	0.12	2.2
6	3.04 (83)	2.70 (96)	2.60 (100)	2.61	2.61	2.61	a:2.60 (-80°C)	>3	—
7	4.69 (21)	4.79 (17.5)	4.85 (15.4)	5.04 (8.6)	5.24 (1.4)	5.27 (0.4)	a:2.48 b:5.28 (-130°C)	-0.37	2.7

* The NCD proportions of 3 and 4 at various temperatures were estimated by using the δ values a:2.34, b:5.20 ppm.

** The presence of 40% NCD isomer was detected at -130 °C.

actual equilibrium in 7 proved to be imposed so far to the opposite direction (Table 2). This unexpected effect of tert-butyl group in raising the enthalpy of the NCD relative to the CHT would be due to the fact that the second sort of non-bonding interaction of 7 is so serious in both A and B that the interaction is not competitively released by the tautomerization of B to A, as compared with the corresponding tautomerization of 5 and 6.

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17) The ^{1}H NMR spectrum of 3,7-dicyano-7-(2-ethoxy-1,3-diphenylcycloprop-2-en-1-yl)norcaradiene, prepared by the cyclopropenylation of 3,7-dicyanocycloheptatriene with 1-ethoxy-2,3-diphenylcyclopropenium ion in the presence of diisopropylamine, shows the signal of H-1,6 at 2.93 ppm, characteristic of the cyclopropyl hydrogen in NCD form (a pale yellow oil, 21%; $\delta(CDCl_3)$ 1.40 (t, $-CH_2C\underline{H}_3$), 2.93 (t, $J_{1,2}=J_{5,6}=3.0$ Hz, H-1,6), 4.58 (q, $-C\underline{H}_2CH_3$), 6.34 (d, $J_{2,4}=$ 2.0 Hz, H-2), 6.76 (m, H-4,5), 7.2-7.7 (m, Ph); MS m/e (%) 376 (M^+ 75), 347 (47), 216 (100); νmax (KBr) 3077, 3045, 2225, 1870, 1603, 1498, 1480 cm^{-1}.

18) The first sort of non-bonding interaction would be more sensitive than the second sort of non-bonding interaction for the bulkiness of the C-7 substituent, therefore a cycloheptatriene carrying a bulky 7-alkyl group would preferably exist in B- rather than in C-type isomer.

19) The ethoxydiphenylcyclopropenyl group of 6 is heavier group than tert-butyl group, but the effective interaction between these groups and H-1,6 would be certainly more serious in 7 than in 6 judging from the molecular model.

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