

# 1,3,5,7-Tetra-*t*-butylbicyclo[4.1.0]hepta-2,4-diene: the First Example of an Alkyl-substituted Norcaradiene in an Equilibrium Mixture with the Cycloheptatriene Tautomer

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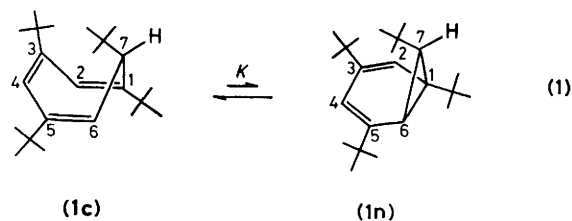
1,3,5,7-Tetra-*t*-butylcyclohepta-1,3,5-triene actually contains its valence tautomer, the norcaradiene form (the title compound) in a ratio of 88.5 : 11.5 at 25 °C, as shown by  $^{13}\text{C}$  and  $^1\text{H}$  n.m.r. spectroscopy, with  $\Delta H^\circ$  and  $\Delta S^\circ$  values of  $+5.3 \pm 0.8 \text{ kJ mol}^{-1}$  and  $+2.0 \pm 2.8 \text{ J K}^{-1} \text{ mol}^{-1}$ , respectively; two kinds of non-bonded repulsive interactions account for the effects of the *t*-butyl groups.

Although various substituents on a cycloheptatriene ring are capable of shifting the cycloheptatriene (CHT)–norcaradiene (NCD) valence tautomerism towards the NCD form,<sup>1–4</sup> no NCD form has been reported to be achieved by the introduction of 'alkyl' substituents alone to cyclohepta-1,3,5-triene. Previously Conrow and his co-workers examined the structures of a series of 2-alkyl-3,7,7-trimethylcyclohepta-1,3,5-trienes by  $^1\text{H}$  n.m.r. and u.v. spectroscopy and concluded that these hydrocarbons exist as cycloheptatrienes.<sup>5</sup> We now report that 1,3,5,7-tetra-*t*-butylcyclohepta-1,3,5-triene (**1**) actually exists as a mixture of CHT–NCD tautomers [(**1c**)  $\rightleftharpoons$  (**1n**)] as shown by low temperature  $^{13}\text{C}$  and  $^1\text{H}$  n.m.r. spectroscopy.

The reaction of 1,3,5-tri-*t*-butyltropylium perchlorate<sup>3</sup> with  $\text{Bu}^t\text{Li}$  in pentane afforded a hydrocarbon mixture. Subjection of this mixture to elution chromatography ( $\text{AgNO}_3$  on  $\text{SiO}_2$ , hexane) followed by t.l.c. ( $\text{SiO}_2$ , hexane) gave (**1**) (20%) and 1,3,6,7-tetra-*t*-butylcyclohepta-1,3,5-triene (**2**) (9%), both as liquids.† Evidence for the valence tautomerism of (**1**) was obtained by observing the  $^{13}\text{C}$  n.m.r. signals of C-1 and C-6 at various temperatures in  $\text{CS}_2\text{-CD}_2\text{Cl}_2$  (3:1 v/v) at 25 MHz (Table 1). At 25 °C C-1 and C-6 exhibited broadened signals at  $\delta$  132.6 and 107.7 p.p.m., respectively. As the temperature was lowered these signals disappeared, and then new signals appeared at  $\delta$  144.3 and 118.2 p.p.m., which were assigned to C-1 and C-6 of (**1c**), respectively. Additionally, a weak signal corresponding to C-1 of (**1n**) appeared at  $\delta$  42.5 p.p.m. at  $-112$  °C.‡ Its intensity was ca. 4% of that exhibited by C-1 of (**1c**), and the signal remained a singlet in an off-resonance spectrum. The C-6 and C-7 signals of (**1n**) were rather difficult to identify because of the intense signals of the four *t*-butyl groups in the expected region, but the weak, somewhat broadened signals at  $\delta$  26.7 and 24.4 p.p.m. may be assigned to C-6 and C-7 of (**1n**), respectively.

The low temperature  $^1\text{H}$  n.m.r. spectrum of (**1**) in  $\text{CS}_2\text{-CD}_2\text{Cl}_2$  (3:1) at 99.55 MHz was also typical of an equilibrium system. The H-6 signal for (**1c**) observed at  $\delta$  4.80 (d,  $J$  9.9 Hz) at 25 °C broadened as the temperature was lowered, and after passing the coalescence point (ca.  $-52$  °C), appeared at  $\delta$  5.15 (d,  $J$  9.5 Hz) at  $-110$  °C. Similar behaviour was also observed for H-7. Unfortunately, it was not possible to identify the H-6 and H-7 signals of (**1n**), presumably owing to overlapping with other signals.

The most characteristic features of the  $^1\text{H}$  n.m.r. chemical shift data of (**1c**) are the exceptional upfield shift of the 7-*t*-butyl signal ( $\delta$  0.66 at  $-110$  °C) and the downfield shift of the H-7 signal ( $\delta$  2.85 at  $-110$  °C). These values are comparable with the  $^1\text{H}$  shift of the 7-*t*-butyl group ( $\delta$  0.75)



(2) = 6-*t*-butyl 5-unsubstituted isomer of (**1c**).

and that of H-7 ( $\delta$  2.60) exhibited by 7-*t*-butyl-1-methylcyclohepta-1,3,5-triene at  $-105$  °C, which contains the 7-*t*-butyl group in an axial orientation.<sup>7</sup> These findings indicate that the 7-*t*-butyl group of (**1c**) is oriented axially owing to its repulsive interaction with the 1-*t*-butyl group, and that the valence tautomerism of (**1**) can be depicted as in equation 1.§

By use of the  $^{13}\text{C}$  chemical shift data for C-1, the equilibrium constant of equation 1 was calculated as 0.130 at 25 °C. Further examination of the C-1 and C-6 shifts at different temperatures in the range  $-5$ — $+40$  °C above the coalescence temperatures in  $\text{CDCl}_3$  yielded  $\Delta H^\circ = +5.3 \pm 0.8 \text{ kJ mol}^{-1}$  and  $\Delta S^\circ = +2.0 \pm 2.8 \text{ J K}^{-1} \text{ mol}^{-1}$ .¶

Previously we reported that the introduction of a *t*-butyl group to the 2- or 3-position of 7-*t*-butyl-7-cyanocyclohepta-1,3,5-triene greatly shifts the CHT–NCD equilibrium to the NCD side, and the effects were attributed to destabilisation of the CHT form due to repulsive interactions between the *t*-butyl group and hydrogen atoms on adjacent carbon atoms.<sup>3</sup> Besides such repulsive interactions around the seven-membered ring, an additional steric factor appears to be at work in the present system (**1**). The 7-*t*-butyl group of (**1c**), which is forced to assume an axial conformation, is considered to interact strongly with the  $\pi$ -electrons of the C-3 double bond. Such repulsive interaction would destabilise (**1c**) and contribute to shift the equilibrium to the (**1n**) side.<sup>9</sup> Since the  $^{13}\text{C}$  n.m.r. spectrum of (**2**), which has a *t*-butyl group at both the 1- and 6-positions, revealed that this exists in the pure CHT form at 25 °C, the presence of a 'single' *t*-butyl group on either the 1- or the 6-position appears essential to give the NCD form. Presumably, the two *t*-butyl

§ In contrast, 7-*t*-butyl-2-methylcyclohepta-1,3,5-triene exists with the 7-*t*-butyl group oriented equatorially<sup>7</sup> as in 7-*t*-butylcyclohepta-1,3,5-triene,<sup>8</sup> and shows the 7-*t*-butyl and H-7 signals at  $\delta$  0.96 and 1.11 at  $-70$  °C, respectively.<sup>7</sup> Although a  $^{13}\text{C}$  n.m.r. spectrum observed at  $-112$  °C in  $\text{CS}_2\text{-CD}_2\text{Cl}_2$  showed no indication for the existence of other tautomers, the time-averaged C-1 and C-6 signals observed in  $\text{CDCl}_3$  sharpened as the temperature was raised to 40 °C and then broadened again at above 55 °C. This suggests the possibility that a small amount of a CHT conformational isomer with the equatorial 7-*t*-butyl group exists in slow equilibrium with (**1c**).

¶ The error limits are based on a 90% confidence level. Complete line-shape analysis by use of 300 MHz  $^1\text{H}$  n.m.r. will be reported in the full paper.

† The two new compounds gave spectral and microanalytical data consistent with their proposed structures.

‡ For comparison, 1,5-di-*t*-butyl-7-cyano-7-methylbicyclo[4.1.0]hepta-2,4-diene shows the C-1 signal at  $\delta$  45.9 p.p.m. at  $-112$  °C.<sup>6</sup>

**Table 1.**  $^{13}\text{C}$  N.m.r. chemical shifts of ring-carbon atoms for the **(1c)**  $\rightleftharpoons$  **(1n)** system in  $\text{CS}_2\text{-CD}_2\text{Cl}_2$  (3:1 v/v).<sup>a</sup>

$t/^\circ\text{C}$	Chemical shift ( $\delta$ )/p.p.m.						
	C-1	C-2	C-3	C-4	C-5	C-6	C-7
25 <sup>b</sup>	132.6 <sup>c</sup>	118.9	146.9	121.8	145.2	107.7 <sup>c</sup>	43.9
-34	— <sup>d</sup>	118.7	146.8	122.0	145.0	— <sup>d</sup>	45.0 <sup>c</sup>
-74	144.8	118.8	147.1	122.5	144.8	118.3	46.7
-112	{ 144.3 42.5 <sup>e</sup>	118.6	146.9	122.5	144.6	{ 118.2 (26.7) <sup>e</sup>	{ 46.4 (24.4) <sup>c,e</sup>

<sup>a</sup> Chemical shifts from  $\text{SiMe}_4$ , measured using a 0.13 M solution; data converted using  $\delta(\text{CS}_2)$  192.2. <sup>b</sup> Methyl carbon atoms at  $\delta$  30.0, 30.4, 30.5, and 31.1 p.p.m., and t-butyl quaternary carbon atoms at  $\delta$  35.5, 35.7, 36.8, and 37.7 p.p.m. <sup>c</sup> Broad signal. <sup>d</sup> Obscured because of line broadening. <sup>e</sup> Signal assigned to **(1n)**.

groups at the 1- and 6-positions in **(2)** repel each other in the NCD form.\*\*

In conclusion, the effects of the t-butyl substituents to shift the equilibrium (equation 1) to the NCD side are accounted for in the first approximation on the basis of two kinds of repulsive interactions characteristic of **(1c)**, which would be partially relieved in **(1n)**, *i.e.*, i, the interactions between 1-t-butyl and H-2, between 3-t-butyl and H-4, and between 5-t-butyl and H-6,<sup>3</sup> and ii, the interaction between the axial 7-t-butyl group and the  $\pi$ -electrons of the C-3 double bond.<sup>9</sup>

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\*\* The marked stability of a similar compound, 2,7-di-t-butyl-4-ethoxycarbonyl-5-methylthiepin, has been attributed to destabilisation of the corresponding thianorcaradiene form due to repulsion between the two t-butyl groups.<sup>10</sup>

## References

- 1 For reviews see, G. Mair, *Angew. Chem.*, 1967, **79**, 446; W. J. le Noble, 'Highlights of Organic Chemistry,' Marcel Dekker, New York, 1974, p. 402.
- 2 T. Mukai, H. Kubota, and T. Toda, *Tetrahedron Lett.*, 1967, 3581.
- 3 K. Takeuchi, M. Arima, and K. Okamoto, *Tetrahedron Lett.*, 1981, 3081.
- 4 K. Takahashi, K. Takase, and H. Toda, *Chem. Lett.*, 1981, 979.
- 5 K. Conrow, M. E. H. Howden, and D. Davis, *J. Am. Chem. Soc.*, 1963, **85**, 1929.
- 6 Unpublished result from this laboratory.
- 7 W. E. Heyd and C. A. Cupas, *J. Am. Chem. Soc.*, 1971, **93**, 6086.
- 8 H. Günther, M. Görlitz, and H.-H. Hinrichs, *Tetrahedron*, 1968, **24**, 5665.
- 9 H. Tsuruta, S. Mori, and T. Mukai, *Chem. Lett.*, 1974, 1127.
- 10 K. Nishino, S. Yano, Y. Kohashi, K. Yamamoto, and I. Murata, *J. Am. Chem. Soc.*, 1979, **101**, 5059.