

# Proton migration on the [60]fullerene cage of 1-*tert*-butyl-1,4-dihydro[60]fullerene to yield the 1,2-isomer

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**Proton NMR data on the base catalysed rearrangement of 1-*tert*-butyl-1,4-dihydro[60]fullerene to the 1,2-isomer reveal a second order reaction and an activation energy of 56.1 kJ mol<sup>-1</sup>.**

It has been reported that treatment of [60]fullerene with *tert*-butyllithium followed by acid quench gives both 1,2- and 1,4-isomers, and that the 1,4-compound rearranges to the more stable 1,2-isomer over a period of 12 h at 25 °C.<sup>1</sup> We now report that the pure 1,4-isomer is indefinitely stable in the solid form (no detectable rearrangement over eighteen months) while even in solution little conversion to the thermodynamic product occurs over two months in deuteriated chloroform. We also show that the rearrangement of the 1,4-isomer to the 1,2-isomer is base catalysed, and provide kinetic and thermodynamic data on this rearrangement.

1-*tert*-Butyl-1,2-dihydro[60]fullerene is the thermodynamically favoured adduct (by *ca.* 12 kJ mol<sup>-1</sup> from PM3 calculations<sup>2</sup>) not requiring (unlike the 1,4-adduct) the introduction of a double bond at the 6,5 ring junction (estimated from similar PM3 parameterisation of the MNDO Hamiltonian to add *ca.* 35 kJ mol<sup>-1</sup>).<sup>3</sup> This unfavourable electronic effect is partly compensated by the absence of the eclipsing (steric) interaction that exists between addenda in the 1,2-position. This factor is clearly demonstrated by increasing the steric requirements of the adducts from Bu<sup>t</sup>Cu<sub>60</sub>H to a bulky 1-*tert*-butyl-1,4-dihydro-2-(3,6-dicyclopropylcyclohepta-2,4,6-trien-1-yl)[60]fullerene, when the 1,4-derivative becomes more favourable by a predicted 75 kJ mol<sup>-1</sup> (also from PM3 calculations).

Maximum yields of 1-*tert*-butyl-1,4-dihydro[60]fullerene were obtained if the reaction was acid quenched within 3 h, using toluene as solvent, and the lithium reagent was added in hexanes. After 24 h only the 1,2-isomer was obtainable. (Up to 85:15 1,4-:1,2-adduct could be obtained). The ratio of the 1,4-:1,2-adducts was not adversely affected when different protic species were introduced *e.g.* water, hydrogen chloride, water-hydrogen chloride, glacial acetic acid or trifluoroacetic acid. In an attempt to form the 1,4-adduct more selectively, the reaction was carried out at elevated temperature (60 °C), but this had little effect, and was not studied in more detail. The proton NMR spectrum of the reaction product shows two *tert*-butyl signals (at  $\delta$  2.08 and 1.88) and two 'cage' proton signals (at  $\delta$  6.67 and 6.32) in CDCl<sub>3</sub>. A NOESY NMR experiment established that the lower field resonance at  $\delta$  6.67 and the *tert*-butyl resonance at  $\delta$  2.08 had a strong transient NOE. We conclude that these resonances represent the 1,2-isomer, which was verified by <sup>13</sup>C NMR.<sup>†</sup> There was no transient NOE between the fullereryl proton and the *tert*-butyl group for the second isomer, ruling out the unfavourable 1,6-adduct.<sup>4</sup>

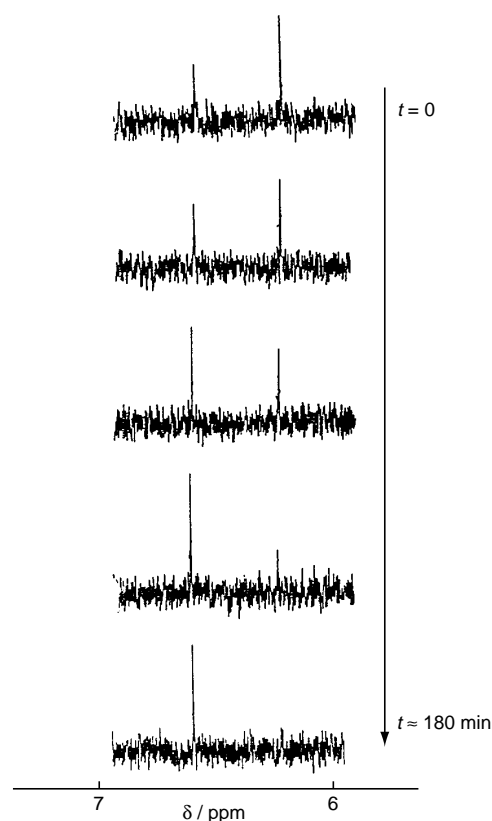
In suitable environments, 1-*tert*-butyl-1,4-dihydro[60]fullerene is stable for prolonged periods of time, but can easily rearrange in the presence of trace impurities. Several acids were explored, but none gave any indication of isomerisation. Treatment of the isomeric mixture with various bases, by contrast, gave an immediate rearrangement reaction.<sup>‡</sup> It is interesting to note that variation of the base showed that the p*K*<sub>a</sub> of the fullereryl (cage) proton of the 1,4-isomer could be crudely estimated at 5.7 > p*K*<sub>a</sub> > 4.15 (these data were

obtained in chloroform or deuteriochloroform solution), a range consistent with other estimates for a variety of such cage protons, and rather higher than that calculated recently (3.31) by quantum mechanical methods.<sup>5</sup>

Experiments were conducted using <sup>1</sup>H NMR as a probe, and perdeuteriated pyridine as base catalyst, reactions being carried out in deuteriochloroform. When deuteriopyridine was added to solutions of the 1,4-isomer, the concentration of the latter was found to decrease, giving an increase in the 1,2-isomer concentration (Fig. 1),§ a *ca.* 96% conversion being generally observed. The 1,4-isomer concentration decayed exponentially with time, and an increase in the concentration of deuteriopyridine increased the rate of reaction.

A linear fit was obtained when the natural logarithm of the concentration of the 1,4-isomer was plotted against time, in agreement with a reaction first order with respect to the fullerene concentration (Fig. 2). A second order reaction was ruled out as a plot of the reciprocal of the substrate concentration with time gave a clearly non-linear relationship (Fig. 2).

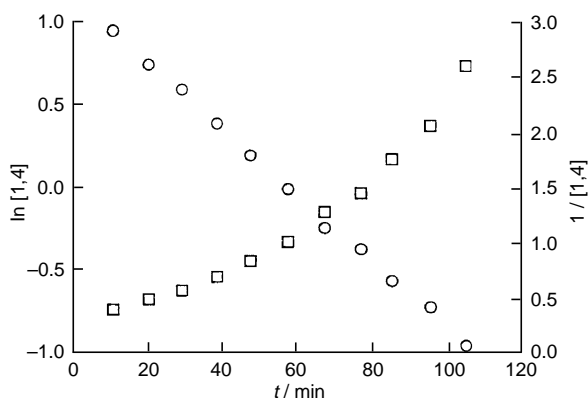
A plot of ln [A]<sub>t</sub> against time allowed us to calculate *k'* at different concentrations of deuteriopyridine (Fig. 3).¶ The results show that the reaction is second order overall and first order with respect to both the concentration of 1,4-Bu<sup>t</sup>C<sub>60</sub>H and deuteriopyridine. The exact value for the rate constant of the



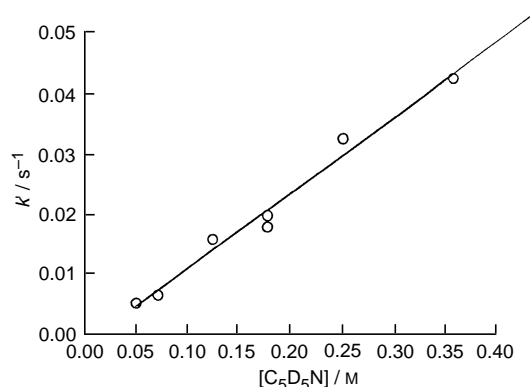
**Fig. 1** Variation of the C<sub>60</sub>H <sup>1</sup>H NMR signals during isomerisation, recorded at 21 ± 1 °C in a 0.35 M solution of C<sub>5</sub>D<sub>5</sub>N in CDCl<sub>3</sub>

reaction  $k_{\text{expt}} [2.1(1) \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}]$ , was calculated from Fig. 3.<sup>¶</sup>

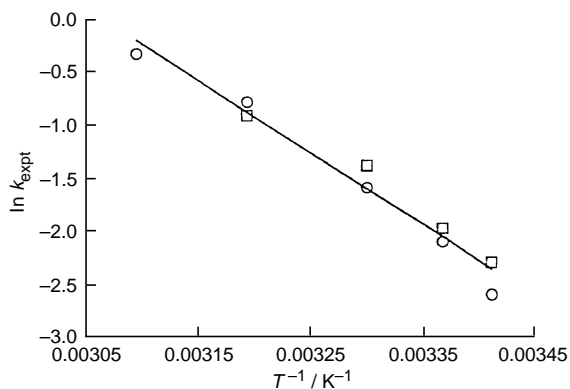
The rate of consumption of the reactant, 1-*tert*-butyl-1,4,-dihydro[60]fullerene, was determined at different



**Fig. 2** First- and second-order plots of the isomerisation reaction of the 1,4-isomer, recorded at  $21 \pm 1^\circ \text{C}$ . First order reaction ( $\circ$ ) plotted vs.  $\ln [1,4]$  (left axis) and second order reaction ( $\square$ ) plotted vs.  $1/[1,4]$  (right axis). Recorded in 0.178.



**Fig. 3** Plot of  $k'$  vs.  $[\text{C}_5\text{D}_5\text{N}]$  at  $21 \pm 1^\circ \text{C}$



**Fig. 4** Arrhenius plot for the isomerisation reaction of the 1,4-isomer in 0.17 ( $\square$ ) and 0.07 m ( $\circ$ )  $\text{C}_5\text{D}_5\text{N}$

temperatures in the range  $20\text{--}50^\circ \text{C}$  for two concentrations. An Arrhenius plot gave an activation energy of  $56.1 \text{ kJ mol}^{-1}$  (Fig. 4).

In an attempt to elucidate the mechanism of the base catalysed reaction, the fullereryl proton was substituted by a deuterium. Similar experiments to those employing  $1,4\text{-Bu}^t\text{C}_{60}\text{H}$  were carried out on the  $1,4\text{-Bu}^t\text{C}_{60}\text{D}$  derivative, again giving a reaction second order overall; first order with respect to  $1,4\text{-Bu}^t\text{C}_{60}\text{D}$  and pyridine. The experimental value for the rate of reaction ( $k_{\text{D}}$ ) was only marginally less than  $k_{\text{expt}}$ , yielding a value of *ca.* 1.2 for  $k_{\text{expt}}/k_{\text{D}}$ .

The mechanism of the hydrogen transfer step is currently under investigation. In initial experiments the  $1,4\text{-Bu}^t\text{C}_{60}\text{D}$  reaction afforded substantially  $1,2\text{-Bu}^t\text{C}_{60}\text{H}$ , the origin of the H atom (possibly adventitious water) and the details of the transfer are being studied.

We thank the authors of ref. 5 for providing details prior to publication.

## Footnotes

† The  $^{13}\text{C}$  NMR spectrum of pure 1-*tert*-butyl-1,2,-dihydro[60]fullerene had 32 resonances indicative of the  $C_s$  symmetry of a 1,2 adduct.

‡ Although the 1,4-isomer is stable as described above, on heating a mixture of the 1,2- and 1,4-isomers at  $60^\circ \text{C}$  for 72 h, up to 25% of the 1,4-isomer rearranges. There may be a concerted, non-catalysed reaction also occurring, albeit at a substantially slower rate than the catalysed reaction. This route of rearrangement will be explored further.

§ Quantitative data were taken, however, from the *tert*-butyl signals, which had a substantially better signal-to-noise ratio.

¶ From the plots we can write eqn. (1) for the overall reaction,



where  $\text{A} = 1,4\text{-Bu}^t\text{C}_{60}\text{H}$  and  $\text{B} = 1,2\text{-Bu}^t\text{C}_{60}\text{H}$ . This gives eqn. (2).

$$\text{rate of reaction} = k_{\text{expt}} [\text{B}][\text{C}_5\text{D}_5\text{N}] \quad (2)$$

If the concentration of deuteriopyridine is kept constant and the decrease in concentration of  $1,4\text{-Bu}^t\text{C}_{60}\text{H}$  is monitored, this gives eqn. (3).

$$-d[\text{A}]/[\text{A}] = k'dt, \text{ where } k' = k_{\text{expt}} [\text{C}_5\text{D}_5\text{N}] \quad (3)$$

Integration of eqn. (3) gives eqn. (4).

$$\ln [\text{A}]_0 - \ln [\text{A}]_t = k't, \quad (4)$$

where  $[\text{A}]_0$  is the concentration of  $1,4\text{-Bu}^t\text{C}_{60}\text{H}$  at  $t = 0$  and  $[\text{A}]_t$  is the concentration of  $1,4\text{-Bu}^t\text{C}_{60}$  at time  $t$ . Eqn. (4) then gives eqn. (5).

$$\ln [\text{A}]_t = -k't + \ln [\text{A}]_0 \quad (5)$$

## References

- P. J. Fagan, P. J. Krusic, D. H. Evans, S. A. Lerke and E. Johnston, *J. Am. Chem. Soc.*, 1992, **114**, 9697.
- T. Kitagawa, T. Tanaka, Y. Takata and K. Takeuchi, *J. Org. Chem.*, 1995, **60**, 1490.
- N. Matsuzawa, D. A. Dixon and T. Fukunaga, *J. Phys. Chem.*, 1992, **96**, 7594.
- A. Hirsch, A. Soi and H. R. Karfunkel, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 766; *Angew. Chem.*, 1992, **104**, 808.
- K. Choho, G. Van Lier, G. Lier, G. Van de Woude and P. Geerlings, unpublished results.

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