Lithium 2-Lithio-1,1,3,3-tetraphenylpropenide[1]

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The novel lithium 2-lithio-1,1,3,3-tetraphenylpropenide (**2**) is shown *via* ^{1}H, ^{13}C, and ^{7}Li n.m.r. spectroscopy and by chemical means to adopt an ionic allyl-lithium structure with C_{2v} symmetry; the second lithium is covalently bonded to the central (C-2) carbon.

The 1,2-addition of alkali metals to activated alkenes is well known.[2] Tetraphenylallene (**1**)[3] is a particularly challenging substrate since its dimetal derivatives are synthetically useful intermediates[4] and can adopt a variety of structures[5,6] (linear or bent arrangement of C-1, C-2, C-3; sp- or sp^2-hybridization of C-2). We have synthesised lithium 2-lithio-1,1,3,3-tetraphenylpropenide (**2**) and describe its unusual structure and reactivity.

The dilithium derivative of tetraphenylallene was prepared *via* reduction of (**1**) with highly active lithium at low temperatures in tetrahydrofuran (THF)† and its structure established from the following: (i) reoxidation with iodine gave the starting material (**1**) whilst protonation with alcohol afforded 1,1,3,3-tetraphenylpropene (**3**); (ii) alkylation of (**2**) with 1,3-dibromopropane, after aqueous work-up, gave (**4**) as the main product; (iii) reduction in liquid ammonia quantitatively transformed (**1**) into lithium 1,1,3,3-tetraphenylpropenide (**5**) which was identified by its ^{1}H and ^{13}C n.m.r. spectra.‡ Compound (**5**) was also accessible *via* deprotonation of (**3**) with n-butyl-lithium in tetrahydrofuran.[7]

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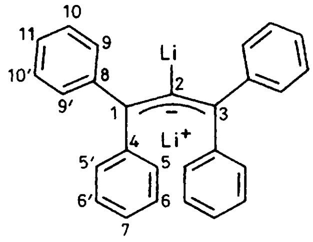
† According to the n.m.r. spectra (**2**) is accompanied by small amounts (3%) of (**5**).

‡ ^{13}C (75 MHz) and ^{1}H (300 MHz) N.m.r. spectroscopic data. δ_C (**2**) ([^{2}H$_8$]THF–[^{2}H$_6$]Me$_2$O, 1:2) −105 °C: 117.9 (C-1, C-3), 204.3 (C-2), 147.6, 150.4 (C-4, C-8), 118.4, 126.0, 126.5, 130.1 (C-5, C-5′, C-6, C-6′), 116.6 (C-7), 129.4 (C-9), 126.5 (C-10), 119.2 (C-11); δ_H (**2**) ([^{2}H$_8$]THF–[^{2}H$_6$]Me$_2$O, 1:2) −120 °C: 7.24, 7.36 (H-5, H-5′), 6.66, 7.04 (H-6, H-6′), 6.43 (H-7), 6.76 (H-9), 6.43 (H-10), 6.22 (H-11); δ_C (**5**) (NH$_3$–THF) −60 °C: 105.0 (C-1, C-3), 132.1 (C-2), 143.8, 148.6 (C-4, C-8), 123.1, 126.6 (C-5, C-9), 125.5, 127.5 (C-6, C-10), 116.0, 117.9 (C-7, C-11); δ_H (**5**) ([^{2}H$_8$]THF) +35 °C: 6.32 (H-2), 6.91 (H-5, H-9), 6.59 (H-6, H-10), 6.29 (H-7, H-11); δ_C (**6**) ([^{2}H$_8$THF) −70 °C: 112.3, 110.6, 107.1 (C-1, C-3, C-4), 43.9 (C-5), 76.2, 76.0 (C-6, C-8), 154.5 q, 150.7 q, 150.3 q, 147.5 q, 130.1, 129.4, 127.9, 127.5, 125.8, 125.4, 123.9, 121.9, 116.8, 116.5, 116.1, 111.9; δ_H (**6**) [^{2}H$_8$]THF +25 °C: 3.10 (H-5), 3.78, 3.88 (H-6, H-8), 6.21 (H-7), 5.89 (H-9), 7.44 d 2H, 7.33 d 3H, 6.98 d 1H, 6.81 m 5H, 6.35 m 4H.

(1)



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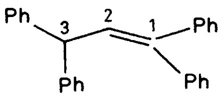

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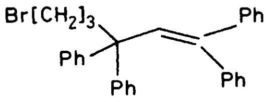

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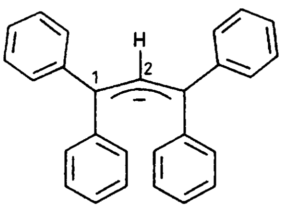

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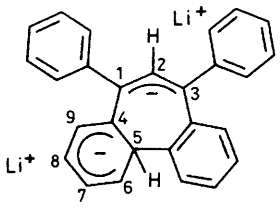

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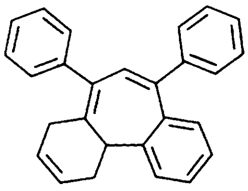

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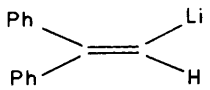

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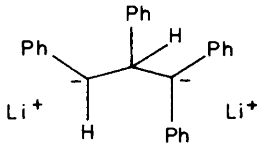

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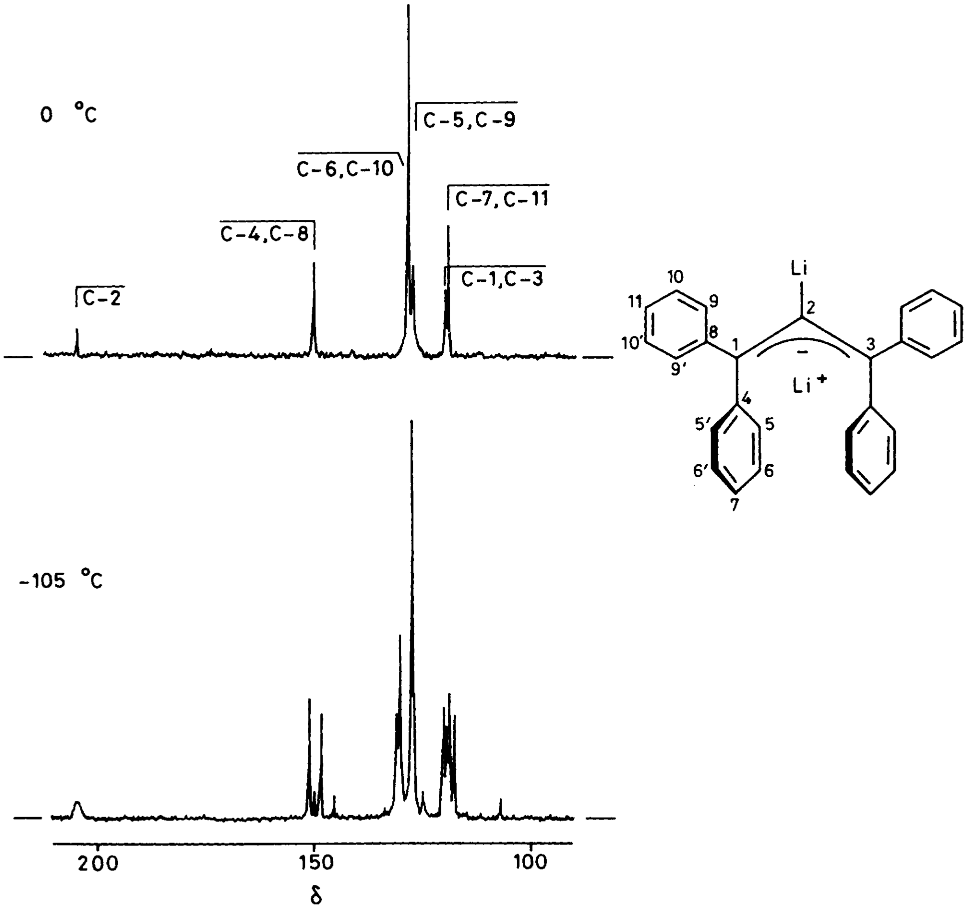

Figure 1. ^{13}C N.m.r. spectra (75 MHz, −105 °C: [^{2}H$_{8}$]THF–[^{2}H$_{6}$]Me$_{2}$O, 1:2; 0 °C: [^{2}H$_{8}$]THF) of (**2**).

Obviously, reduction of (**1**) in liquid ammonia was accompanied by protonation; (iv) anion (**2**) rearranged irreversibly into dianion (**6**) at temperatures above 0 °C.‡ Protonation of (**6**) afforded the dihydroderivative (**7**).[8]

The n.m.r. spectroscopic description of (**2**) (see Figure 1)‡ leads us to the following conclusions. (i) Anion (**2**) is similar to (**5**) in that it possesses a bent (C_{2v}) structure in which the two *endo*- and *exo*-phenyl groups are pairwise equivalent. (ii) The broad resonance of C-2 (-105 °C: $w_{\frac{1}{2}} = 130$ Hz) and the sharp resonance of C-1 (C-3) of the title compound (**2**) are downfield from those of (**5**) by 72.2 and 12.9 p.p.m., respectively. There is a coupling between C-2 and a quadrupolar ^{7}Li-nucleus due to a covalent bond (see below). In dealing with the absorption of C-2 at such an extremely low field the structurally related 1,1-diphenyl-2-lithioethene (**8**) was prepared as a model compound by lithiation of the corresponding bromide with t-butyl-lithium.[9] In (**8**) the metallated carbon atom resonates at δ 193.0, *i.e.* 78.9 p.p.m. downfield from the corresponding hydrocarbon resonance. (iii) The downfield (high field) absorptions of C-2 (C-1, C-3) together with the pronounced shielding of the *para*-carbon atoms of the phenyl groups (C-7, C-11) indicate a π-charge distribution to the non-bonding allyl π-orbital and a significant delocalization of the charge into the phenyl rings.

Thus, the reductive formation of the anion (**2**) can formally be described as the 1,2-addition of lithium to a C=C-double bond of the allene. One lithium becomes involved in an ionic allyl-lithium structure while the other is part of a strongly polar, covalent C-2–Li bond orthogonal to the π-system. An alternative C_{2v}-type structure with two 'Li-bridges' between C-1 and C-3 above and below the plane through C-1, C-2, C-3[6] cannot be rigorously excluded, but appears much less likely because of the above spectroscopic findings.

Both (**2**) and the related anion (**5**) exhibit remarkable stereodynamic behaviour. It appears from the ^{13}C n.m.r. spectra of (**2**) and (**5**) at -105 °C (two pairs of phenyl groups) that the rotation about the C-1–C-2 (C-2–C-3) bond is slow on the n.m.r. time scale. Moreover, the *ortho*- (*meta*-) carbon atoms of two phenyl rings of (**2**) are no longer equivalent. This must be due to a slow rotation of these phenyl groups. It is reasonable to identify the two phenyl units as the *endo*- rings whose rotation is inhibited by considerable steric hindrance. The low-temperature spectra provide no evidence for a slow rotation of the phenyl rings in (**5**) or for a non-equivalence of the position C-1 and C-3 in (**2**). The non-equivalence would result from a partial covalent bonding between the metal and one of the terminal carbon centres. The detection of one broad (-105 °C: $w_{\frac{1}{2}} = 45$ Hz) ^{7}Li signal at δ -0.1 (LiCl–H_2O, ext.) could be due to intra- or inter-molecular exchange effects. It is noteworthy that the ^{13}C resonance of C-2 in (**2**) sharpened upon warming to 0 °C.

The ^{13}C and ^{1}H n.m.r. spectra of (**2**) and (**5**)[7] at ambient temperatures [only three ^{1}H n.m.r. resonances due to the phenyl protons at 0 °C (**2**) and 35 °C (**5**), respectively] indicate the existence of four equivalent phenyl groups. We conclude that both the rotation of the phenyl rings around the C-1–C-4 and C-1–C-8 bonds and the rotation around C-1–C-2 (C-2–C-3) bond (with partial π-bond character) are rapid on the n.m.r. time scale.

In order to obtain another model compound for (**2**) we treated (**3**) with lithium at low temperatures. There is no cleavage of the C-3–H bond. However, the initially formed dianion undergoes a 1,2-migration of the phenyl group at C-3 to afford the dianion (**9**).

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