lamp photolysis of t_R but the standard deviation is very large. The two log plots in fact generate curved rather than straight lines. The most likely explanation for why the log plots are not linear is that with the high powered pulsed laser the conditions necessary to make the photochemical steps first-order in substrate concentration – low absorbance by the solution – do not hold.¹¹

In conclusion, we have shown that the *cis*–*trans* isomerization of **t** and **c** may be more complicated than previously suspected. A plausible, but by no means exclusive, explanation is that the chiral perpendicular intermediates interconvert directly. Another possibility is that two mechanisms of isomerization, *e.g.*, the one described in equation (2) and the one involving the carbene cyclooctanylidene, occur simultaneously. Further experimental and theoretical research will be required to test these hypotheses.

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Generation and stereocontrolled trapping of 3-phenylcyclopropene and its derivatives

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Selective methods for the preparation of 3-phenylcyclopropene and its 1-substituted derivatives are provided. The parent cyclopropene is readily trapped in (3+2)- and (4+2)-cycloadditions that lead to *exo*-3-phenyl-1,2-disubstituted cyclopropanes. *Ab initio* calculations suggest that the lowest energy conformation has the plane of the benzene ring perpendicular to the cyclopropene π -bond but with a low rotation barrier.

The unusual geometry and high strain energy of both saturated and unsaturated three-carbon rings^{1,2} and the ability of substituents to change their structural parameters,³ the regiochemistry of their reactions and, correspondingly, their biological properties are of interest to synthetic chemists, theoreticians and biochemists.^{4–10} Cyclopropane and cyclopropene derivatives^{11,12} are useful building blocks for syntheses. Cyclopropene itself, although stable indefinitely as a solid at liquid nitrogen temperature, and relatively stable at 325 °C diluted with helium,¹³ undergoes dimerisation through an ene-reaction or oligomerisation even at –78 °C in a condensed phase.¹³ Despite the enormous growth in the understanding of the chemistry of cyclopropenes, relatively little has been reported concerning systems having no substituents on the double bond and only one substituent at C-3. Indeed, although a number of examples have been reported, only 3-methylcyclopropene has been widely studied.¹⁴ We consider the chemistry of 3-phenylcyclopropene **1**,¹⁵ and its derivatives **2–5**.[†]

The initial precursor was 1,1,2-tribromo-3-phenylcyclopropane **6**, which was prepared as an *E/Z*-mixture from cinnamaldehyde

by protection as the diethylacetal derivative followed by dibromocyclopropanation under phase-transfer conditions. Subsequent deprotection and oxidation of the aldehyde gave 2,2-dibromo-3-phenylcyclopropanecarboxylic acid. This acid was converted into tribromide **6** under Hunsdiecker conditions.[‡] Reaction of **6** with 1.1 equiv. of methylolithium led to 1,2-dehalogenation with the formation of 1-bromo-3-phenylcyclopropene **4**,¹⁶ which could be trapped if the reaction was carried out in the presence of diphenylisobenzofuran (DPIBF) as the *exo-anti*-adduct **11**.[§] In the absence of the trap, the cyclopropene rearranged over 18 h at –30 °C to a mixture of allene **7** and acetylene **8**. Similar rearrangements have been reported for other monohalocyclopropenes.¹⁷

If the tribromide **6** was treated with 2.2 equiv. of MeLi at –80 °C, allowed to reach room temperature for 30 min, quenched with water or methanol at –40 °C and then concentrated at

[†] Low resolution mass spectra were measured using a Finnigan 8430 spectrometer with EI 70 eV unless otherwise stated. Accurate mass measurements refer to ⁷⁹Br isotopes unless stated and were carried out on a MicromassTM GCT spectrometer. Microanalyses were performed on a Carlo Erba Model 1106 CHN analyzer. NMR spectra were recorded in CDCl₃ using Bruker AC250 and A500 spectrometers at 250 or 500 MHz (¹H) and 62.9 or 125 MHz (¹³C). IR spectra were obtained in CHCl₃ solutions or as liquid films on a Perkin-Elmer 1600 FTIR spectrometer.

[‡] Compound **6**, a mixture of two stereoisomers (*trans/cis* = 5): a colourless oil (found, M⁺: 353.8076; C₉H₇⁷⁹Br₂⁸¹Br requires: 353.8077).

trans-Isomer, ¹H NMR, δ : 2.99 (d, 1H, *J* 7.0 Hz), 3.88 (d, 1H, *J* 7.0 Hz), 7.26–7.41 (m, 5H). ¹³C NMR, δ : 33.2 (CH), 33.7 (C), 45.3 (CH), 128.3 (CH), 128.5 (CH), 128.6 (CH), 134.0 (C).

cis-Isomer, ¹H NMR, δ : 3.04 (d, 1H, *J* 9.8 Hz), 4.11 (d, 1H, *J* 9.8 Hz), 7.26–7.55 (m, 5H). ¹³C NMR, δ : 31.6 (CH), 36.7 (CH), 37.7 (CH), 128.0 (CH), 128.2 (CH), 130.2 (CH), 132.6 (C).

Scheme 1

–20 °C, it gave 3-phenylcyclopropene **1** in 35 % yield, as determined by ^1H NMR.[†] This was trapped on addition of DPIBF as a single adduct, **10** (70% based on **6**).[‡]

Scheme 2

Cyclopropene **1** decomposed completely after a week in a CDCl_3 solution; no clear products could be identified. However, it could also be trapped efficiently in a range of other cycloadditions. In the case of the Diels–Alder adducts **10** and **13–15** with diphenylisobenzofuran, furan and isoprene, in each case the phenyl substituent was *exo*- on the cyclopropane ring. Similar selectivities have been observed for reactions of 3-methyl-3-phenylcyclopropene with DPIBF.¹⁸ In contrast, this alkene forms *endo*-cycloadducts with up to 80 % selectivity, or exclusively in the case of *o*-benzoquinone, in reactions with cyclones.¹⁸ With compound **1** the adducts with diazomethane and benzonitrile oxide also had the *exo*-stereochemistry.

Ab initio calculations at the B3LYP/6-31G* level suggest that 3-phenylcyclopropene **1**, like the 3-methyl-3-phenyl system, has a preferred bisected conformation; the rotation barrier for cyclopropene **1** is calculated to be 13.7 kJ mol^{–1}, whereas that for the 3-methyl-3-phenyl system is lower at 5.6 kJ mol^{–1}.¹⁸ This probably reflects the lower stability of the bisected geometry

[§] This was a white powder, mp 157–159 °C (MeOH) (found, M^+ : 464.0757; $\text{C}_{20}\text{H}_{21}^{79}\text{BrO}$ requires: 464.0776). ^1H NMR, δ : 2.50 (d, 1H, J 4.4 Hz), 3.85 (d, 1H, J 4.4 Hz), 7.19 (m, 1H), 7.25–7.55 (m, 14H), 7.69 (m, 2H), 7.85 (m, 2H). ^{13}C NMR, δ : 37.3 (CH), 38.4 (CH), 50.9 (C), 89.1 (C), 92.4 (C), 119.8 (CH), 122.6 (CH), 126.5 (CH), 127.0 (CH), 127.2 (CH), 127.9 (CH), 128.2 (CH), 128.59 (CH), 128.62 (CH), 128.8 (CH), 128.9 (CH), 129.3 (CH), 129.6 (CH), 133.1 (C), 135.1 (C), 136.8 (C), 147.7 (C), 148.7 (C). IR (CHCl₃, ν_{max} /cm^{–1}): 3061 (m), 3029 (m), 1605 (m), 1497 (s), 1449 (s), 1304 (s), 1217 (s), 981 (s), 910 (w), 749 (s), 696 (s).

[†] 3-Phenylcyclopropene **1**. ^1H NMR, δ : 2.7 (s, 1H), 7.1–7.3 (m, 7H). ^{13}C NMR, δ : 19.5 (CH), 108.6 (CH), 125.6 (CH), 128.0 (CH), 128.6 (CH), 147.1 (C). IR (film, ν_{max} /cm^{–1}): 1646 (s). Phenylcyclopropene **1** was trapped on the addition of DPIBF (1.0 equiv.) as single adduct **10** (70%, based on tribromide **6**), a white powder, mp 156–158 °C (MeOH) (found, M^+ : 386.1669; $\text{C}_{20}\text{H}_{22}\text{O}$ requires: 386.1671). ^1H NMR, δ : 2.20 (d, 2H, J 3.2 Hz), 3.30 (t, 1H, J 3.2 Hz), 7.11–7.76 (m, 19H). ^{13}C NMR, δ : 33.1 (CH), 35.2 (CH), 89.6 (C), 119.5 (CH), 126.1 (CH), 126.3 (CH), 126.4 (CH), 128.3 (CH), 128.40 (CH), 128.43 (CH), 128.6 (CH), 136.1 (C), 140.1 (C), 150.2 (C). IR (CHCl₃, ν_{max} /cm^{–1}): 3061 (m), 3030 (m), 1954 (w), 1810 (w), 1604 (m), 1497 (m), 1454 (s), 1342 (w), 1307 (s), 1248 (w), 1217 (m), 1059 (w), 981 (s), 905 (m), 747 (s), 698 (s).

Scheme 3

caused by the introduction of the methyl group. In support of this, calculations for 3-*tert*-butyl-3-phenylcyclopropene suggest a preferred geometry in which the plane of the benzene ring is parallel to the cyclopropane π -bond. The HOMO of the preferred conformation of **1** is shown in Figure 1, alongside the calculated minimum energy structure.

Attempts to trap the intermediate 1-lithio-3-phenylcyclopropene **9** by the addition of acetone or benzaldehyde to the carbonyl group gave a good yield of cyclopropen-1-yl carbinol **3** in the former case^{††} and no adduct in the latter. However, it could be trapped by reaction with methyl iodide at room temperature for 9 h, giving compound **2** in 53% yield.^{‡‡} Trapping with methyl chloroformate or carbon dioxide led only to apparent polymers. However, reaction with TMSCl did give unstable cyclopropene **5**, which could be trapped in 30% yield by reaction with DPIBF, **12**.^{§§}

Thus, efficient procedures have been developed for the preparation of 3-phenylcyclopropenes allowing the effect of the substituent on the reactivity of the cyclopropane π -bond to be studied.

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Figure 1

^{††} This was stable for 3 weeks at –20 °C. The product contained some 4-hydroxy-4-methylpentan-2-one formed in the reaction conditions from acetone.

^{‡‡} Compound **2** was stable for two weeks at –20 °C when neat and for several months at that temperature in ethereal solution.

^{§§} Compound **5**, a colourless oil. ^1H NMR (–40 °C) δ : 0.28 (s, 9H), 2.61 (s, 1H), 7.17–7.56 (m, 6H). ^{13}C NMR, δ : –1.3 (SiMe₃), 20.2 (CH), 116.7 (C), 119.6 (CH), 124.7 (CH), 125.0 (CH), 127.7 (CH), 148.4 (C). IR (film, ν_{max} /cm^{–1}): 3059 (w), 3025 (m), 2955 (s), 2897 (m), 1693 (s), 1602 (m), 1492 (m), 1446 (s), 1407 (w), 1248 (s), 1070 (w), 841 (s), 756 (s), 698 (s). An optimised synthesis of this cyclopropene, as well as its unusual dimerisation, will be described elsewhere.

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Supernova antineutrino interactions cause chiral symmetry breaking and possibly homochiral biomaterials for life

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There is some evidence that non-racemic hydrocarbons occur in meteorites. This would indicate an extraterrestrial origin of the homochirality in living systems (proteins, DNA and RNA). The weak interaction breaks chiral symmetry but a robust process is needed. We propose that an SNII explosion antineutrinos could provide this mechanism in the solar cloud. Pre-simple estimates of this possibility are given here.

Homochirality of Life. For more than a century, there has been evidence for the chiral nature of life forms on Earth. Pasteur was among the first to point this out (1848–1880), and the universal nature of chiral symmetry breaking in DNA and RNA is now very well established for all life forms. Figures 1 and 2 show how the homochirality is manifested at the molecular level.

With the discovery of parity violation in charged current reactions in 1956 and of the weak neutral currents (WNCs) in 1973, two universal symmetry-breaking processes (WNC and β -decay) were uncovered that could have determined the handedness in DNA and RNA. The main problem is the extremely small symmetry-breaking effects ($\Delta E/k_B T \sim 10^{-17}$). However, there are plausible non-linear mechanisms that could have amplified this small symmetry-breaking phase transition up to the full symmetry-breaking level observed in life forms. There is, nevertheless, a long-standing controversy as to whether these non-linear effects are actually large enough to have determined the selection of the handedness of life.^{1–11}

For many years, there have been several issues associated with the homochiral structure of biomolecules, as first observed by L. Pasteur in 1848:

- (a) Is a homochiral structure necessary for life as we know it?
- (b) Did homochirality precede the formation of life (homochiral prebiotic medium hypothesis)?
- (c) Is there any reasonable physical mechanism that could have produced the large chiral symmetry breaking the prebiotic medium or in the observed homochiral structure?
- (d) Is the homochiral structure an accident that occurred in the biological systems and was later amplified?
- (e) Can the homochirality be used as a signature for existing or previous living systems in the solar system or other parts of our galaxy?
- (f) Are there any experiments than can be carried out now to clarify the origin of homochirality?

Recently, there has been increasing interest in the chiral nature or handedness of biomolecules. In fact, there are some who claim that the complex biomolecular structure of life must have arisen from a ‘chiral pure’ medium^{12,13} and may be a precondition for the emergence of self-replicating biomolecular systems. Table 1 lists some of these ideas, which have been put forward largely by W. Bonner and V. Goldanskii.^{12,13} We also point out a recent review¹⁴ (see also ref. 15 for more recent details). This concept, combined with the likelihood that the period on Earth for life to have originated seems to be sometime between 3.8 and 3.5 billion years ago, leaves a small window of 300 million years or less for life to have emerged from the prebiotic medium. Indeed, some speculate that the time could be less than 10 million years.

We now turn to the experiments that study possible asymmetry processes. Over the past 20 years, many experiments have been carried out (see ref. 12 for a nearly complete list). However, it appears that nearly every positive effect that was observed has turned out to be incorrect. In Table 2, we list experimental results that are not yet refuted or in direct conflict with previous null effects. The observation that circularly polarised light destroys L and D isomers selectively (Table 2, entry 1) is now well established.

The other experiment to which we will refer is that of entry 2 (Table 2), the study of Cherenkov light in L or D material with chiral e^- (β -decay).²⁰ The authors claim an effect of perhaps

Table 1

1. DNA: Self replication would not work with heterochiral systems (50% L and 50% D).
2. Errors in DNA replication: Without a pure chiral structure, the error rate in replication would be unacceptable to long-lived systems (higher animal forms, trees etc.).
3. In a prebiotic medium: Homochirality must have been either (A) established in a very short time on earth (≤ 100 Myr), or, (B) existed in ISM organic materials near the solar system