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Generation and stereoselective transformations of 3-phenylcyclopropene

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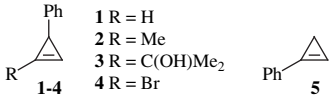
ABSTRACT

A convenient and inexpensive approach to the generation of 3-phenylcyclopropenes is described. Reaction of these compounds with a range of dienophiles and dipolarophiles led to the stereoselective formation of [4+2]- and [3+2]-cycloadducts, which were exclusively *exo*-3-phenyl-*cis*-1,2-disubstituted cyclopropanes. Efficient trapping of 1-lithio-3-phenylcyclopropene with different electrophiles is also discussed. *Ab initio* calculations suggest that the lowest energy conformation of 3-phenylcyclopropene has the plane of the benzene ring perpendicular to the cyclopropene π-bond but with a low rotation barrier.

1. Introduction

The unusual geometry and high strain energy of cyclopropanes and cyclopropenes,[1,2] and the ability of substituents to cause subtle changes in their structural parameters,[3] in the regiochemistry of their reactions and in their biological properties are of interest to synthetic chemists, theoreticians and biochemists.[4–14] Cyclopropane and cyclopropene derivatives are valuable building blocks for organic synthesis.[15,16] For instance, cycloaddition reactions of cyclopropenes are useful in the synthesis of bi- or polycyclic systems having a cyclopropane moiety in their skeleton,[17] including natural compounds and their analogues.[18] Cyclopropene itself, although stable indefinitely as a solid at liquid nitrogen temperature and relatively stable at 325 °C diluted with helium,[19] undergoes dimerisation through an ene-reaction or oligomerisation even at −78 °C in a condensed phase.[20]

Despite the enormous growth in the understanding of the chemistry of cyclopropenes, there is still a lack of knowledge of the chemistry of cyclopropenes with an unsubstituted double bond that have a single substituent at C-3. Although a series of such cyclopropenes has been obtained,[21] only the chemistry of 3-methylcyclopropene has been widely studied.[22] Moreover, relatively little has been reported of any cyclopropenes bearing just a single aryl substituent. There is one report of the generation and trapping of the very unstable 1-phenylcyclopropene **5**, derived from 1,1,2-tribromo-2-phenylcyclopropane.[23] Therefore the aim of the present work was to develop an effective approach to 3-phenylcyclopropene **1** and its derivatives (Scheme 1). Initial results in this area have been represented in a short communication,[24] we now provide the details.



Scheme 1.

2. Results and discussion

Two possible synthetic pathways to the target phenylcyclopropenes have been chosen based on the literature: the reaction of a monobromocyclopropane with *tert*-BuOK,[25] and reaction of a 1,1,2-tribromocyclopropane with alkyllithium.[26]

In the first of these, dehydrobromination of stereoisomeric 1-bromo-2-phenylcyclopropanes **6** was carried out under standard conditions (*tert*-BuOK, THF).[25,26a] This formed exclusively 1-phenyl-*cyclo*-propene **5**, which was trapped with 1,3-diphenylisobenzofuran (1,3-DPIBF) giving the adduct **7** in 77% yield (Scheme 2). Dehydrobromination of **6** did not take place at −40 °C and proceeded slowly at −20 to −10 °C.

No traces of the adduct of 3-phenylcyclopropene **1** with 1,3-DPIBF (**19**, see below) were observed in the reaction mixture by ^{1}H NMR spectroscopy; this showed the absence of 3-phenylcyclopropene among the reaction products. This might be explained in terms of

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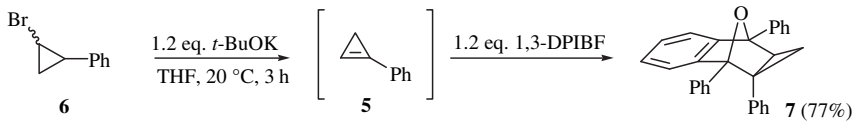


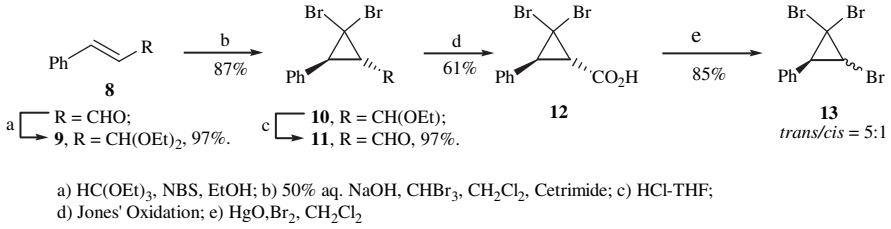
Scheme 2.

selective deprotonation of the CHPh fragment due to the higher acidity of its proton compared to the one of CH_2-group protons. Carrying out the above reaction in DMSO in the absence of a trap led to a complex mixture of undefined products. Only (*E*)-1-phenylbutadiene-1,3 was isolated from the mixture, in 7% yield. Nonetheless, the above approach to 1-phenylcyclopropene (Scheme 2) can be carried out on a large scale and may have advantages compared to those reported before,[23,27] which require low temperatures and the use of organolithium reagents.

To exploit the second approach to 3-phenylcyclopropene **1**, 1,1,2-tribromo-3-phenylcyclopropane **13** was prepared as an *E*/*Z*-mixture from *trans*-cinnamaldehyde **8** by protection as the diethylacetal derivative **9** followed by dibromocyclopropanation under phase-transfer conditions. Subsequent deprotection of **10** and further oxidation of the aldehyde **11** gave 2,2-dibromo-3-phenylcyclopropane carboxylic acid **12**. This acid was converted into tribromide **13** under Hunsdiecker conditions (Scheme 3) with 43% overall yield from **8**.

The stereochemistry of the adducts **16** and **17** was established based on the NMR data and was in accordance with those reported for [4+2]-cycloaddition reactions of cyclopropenes: *exo*-addition in case of 1,3-DPIBF[28] and *endo*- in the case of cyclopentadiene.[29] In particular, the chemical shift of benzylic proton H-3 (3.85 ppm for **16** and 2.31 ppm for **17**) was quite characteristic and served as evidence of *exo*- and *endo*-stereochemistry of compounds **16** and **17**, respectively. The *anti*-orientation of the phenyl substituent in molecules of **16** and **17** was proved by the *trans*-stereochemistry of the cyclopropane protons, which was determined based on the low values of their coupling constants, 4.4 and 4.3 Hz, respectively.

If the tribromide **13** was treated with 2.2 mol equiv of MeLi at −80 °C, allowed to reach rt for 30 min, then quenched with water or methanol at −40 °C and subsequently concentrated at 20 °C, it gave 3-phenylcyclopropene **1**[30] in 35% yield, as determined by ^{1}H NMR spectroscopy (Scheme 5). Addition of 1,3-DPIBF to **1** allowed it to be trapped as a single adduct **19** (5 min, 20 °C, complete conversion). Cyclopropene **1** decomposed rapidly when concentrated perhaps by oligomerization; its 3%-$CDCl_3$ solution decomposed completely after a week and no clear products could be identified.

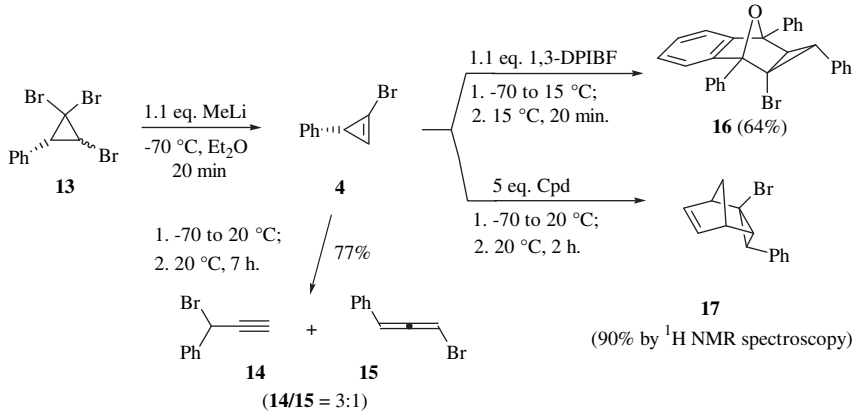


a) $HC(OEt)_3$, NBS, EtOH; b) 50% aq. NaOH, $CHBr_3$, CH_2Cl_2, Cetrimide; c) HCl-THF; d) Jones' Oxidation; e) HgO,Br_2, CH_2Cl_2

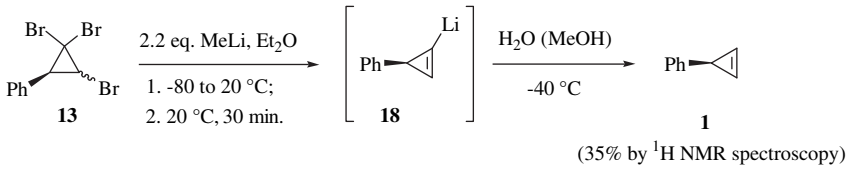
Scheme 3.

It is known that 1,1,2-tribromocyclopropanes readily react with 1.0–1.2 equiv of an alkyllithium at low temperature to give 1-bromocyclopropenes.[26] The reaction of tribromide **13** with 1.1 mol equiv of MeLi led to cyclopropene **4**, which underwent complete rearrangement over 18 h at −30 °C (or 7 h at 20 °C) to give a mixture of acetylene **14** and allene **15** (Scheme 4). Similar rearrangements have been reported for other monohalocyclopropenes.[6,16] Generation of bromocyclopropene **4** in situ in the presence of 1,3-DPIBF or cyclopentadiene (Cpd) led to the products of its trapping as corresponding [4+2]-cycloadducts **16** and **17** in good yields (Scheme 4).

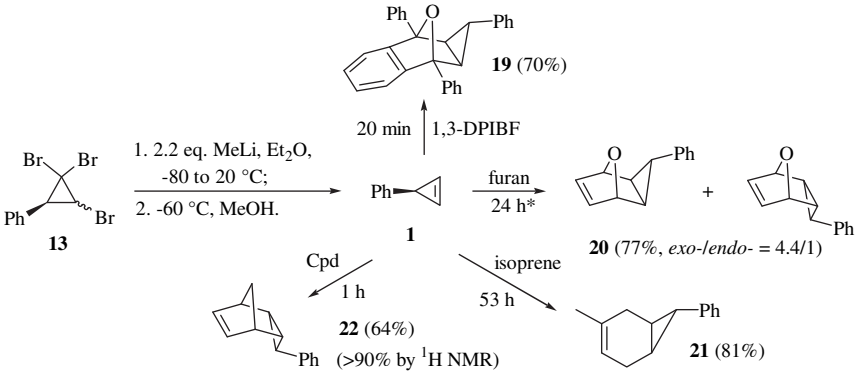
Generation of 3-phenylcyclopropene from tribromide **13** in situ allows its use as a valuable synthon in the stereoselective synthesis of carbo- and heterocyclic compounds based on [4+2]- and [3+2]-cycloaddition reactions. The cyclopropene was generated in ether from **13** and 2.2 mol equiv of MeLi with subsequent MeOH work up at −60 °C followed by the addition of the corresponding dienes. [4+2]-Cycloadducts **19**–**22** were obtained under mild conditions (ether, 20 °C) from 1,3-dienes (furan, isoprene, 1,3-DPIBF and



Scheme 4.



Scheme 5.



* In all cases it is shown: a) time of stirring of reaction mixture at r.t.; b) isolated yield of adducts based on **13**.

Scheme 6.

cyclopentadiene) and **1** in good yields (Scheme 6). The above conditions minimized oligo- and polymerization of **1** and allowed efficient and selective trapping of the highly reactive cyclopropene in [4+2]-cycloaddition reactions with a variety of reagents.

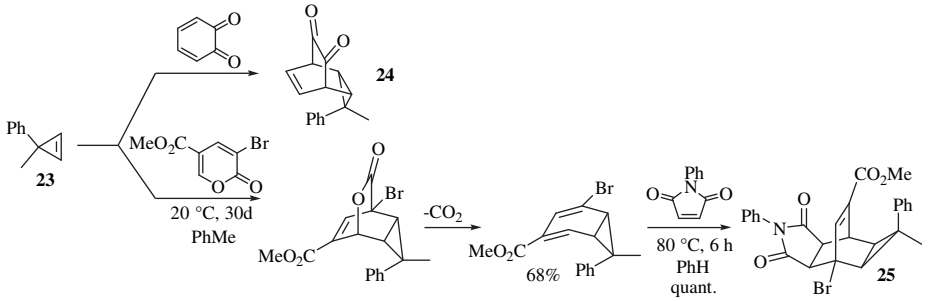
In each of the Diels–Alder adducts **19**–**22** with 1,3-DPIBF, furan, isoprene and Cpd, the phenyl substituent was *anti*-oriented to the other cyclopropane substituents. Similar selectivities have been observed for reactions of 3-methyl-3-phenylcyclopropene **23** with 1,3-DPIBF.[31] The *anti*-stereochemistry of the phenyl substituent in the adducts **19**–**22** was established based on the *J* values of *trans*-oriented cyclopropane protons equal to 3.2 Hz for **19**, 4.7 and 4.4 Hz for **21** and 0 Hz for **22**.

The isomers *exo*-**20** and *endo*-**20** were separated by chromatography and characterized by ^{1}H and ^{13}C NMR spectroscopy. The *anti*-orientation of the phenyl substituent in the adducts **20** was established based on the values of coupling constants $J_{2,3}$. The configurations of the two isomers could be determined based on the chemical shifts of H-3 in their ^{1}H NMR spectra. The proton H-3 in the molecule of *endo*-**20** is shielded by the double bond, thus its signal is shifted to higher field compared to H-3 of the *exo*-**20**.[28] On the other hand H-3 in *exo*-**20** is deshielded due to the influence of the oxa-bridge and should be shifted to a lower field. This leads to the observed difference in the chemical shifts of H-3 in the molecules of *endo*- and *exo*-**20** of 0.89 ppm.

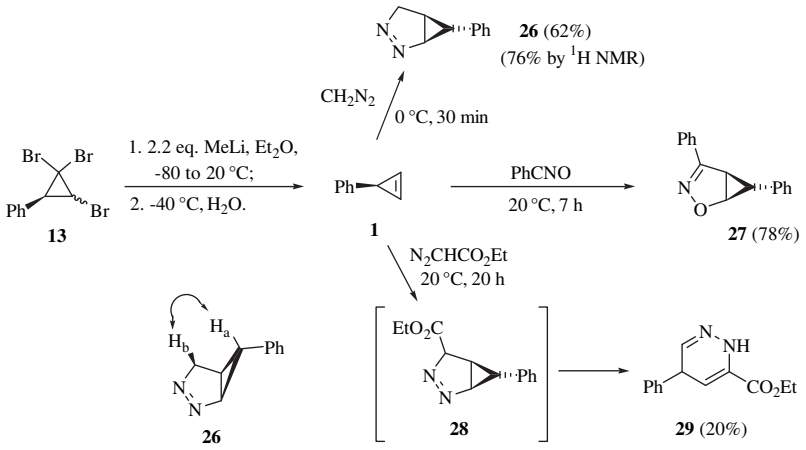
The above assignment was confirmed based on the results of NOESY experiments. Thus, the *endo*-configuration of **20** was established based on the correlation peak H^3/H^4, while there was no such peak in the spectra of *exo*-**20**. On the other hand, the spectra of both *exo*- and *endo*-**20** contain cross-peaks H^2/*o*-**Ph** confirming the *cis*-orientation of H^2 and the phenyl group in the cyclopropane that in turn is possible only in case of *anti*-orientation of the phenyl substituent relative to the bicyclic system (Scheme 7).

Scheme 7.

The *anti*-phenyl orientation in these adducts is the opposite of that in adducts of 3-methyl-3-phenylcyclopropene **23** with e.g., electrophilic *o*-benzoquinone (**24**) and [2*H*]-pyran-2-ones (**25**) (Scheme 8) and with nucleophilic isoprene, cyclopentadiene, furan and 1,3-DPIBF.[31]



Scheme 8.

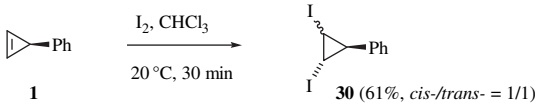


Scheme 9.

3-Phenylcyclopropene **1** appeared to be a reactive dipolarophile. When used for [3+2]-cycloadditions[16,17] with diazomethane, benzonitrile oxide and ethyl diazoacetate, it was generated from tribromide **13** and MeLi with subsequent water work up at −40 °C (Scheme 9). The pale-orange ethereal solution of **1** obtained was warmed up to 0 °C, rapidly washed with water, dried and concentrated at 20 mmHg to ~2% solution, then immediately treated with the dipolar species. The good yields of the cycloadducts **26** and **27** show that at the time of 1,3-dipolar reagent addition the amount of **1** present was not less than 80% based on the starting tribromide **13**. Product **29** was formed by the intramolecular rearrangement of the initially formed [3+2]-cycloadduct **28**,[32] which was not detected in the crude mixture. The low yield of product **29** could be the result of the low rate of the reaction of ethyl diazoacetate with 3-phenylcyclopropene; thus, the cyclopropene decomposed during the reaction as seen by NMR spectroscopy after 20 h at rt, which showed the complete consumption of **1** and unreacted diazo-component.

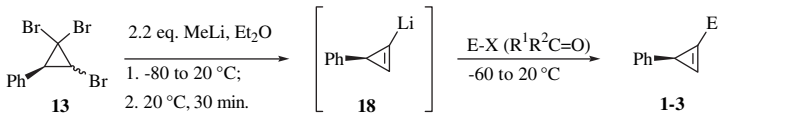
The [3+2] adducts of **1** with diazomethane and benzonitrile oxide also had the *exo*-stereochemistry of the phenyl group. For **26** this was established based on NOESY data, which showed the spatial closeness between the protons H_a and H_b (Scheme 9). The *anti*-orientation of the phenyl substituent in **27** was determined based on the *J* values (3.2 and 1.9 Hz) of the benzylic proton (δ 1.85 ppm).

It is known that electrophilic addition of iodine to cyclopropenes can be used as an effective protection of the double bond.[33] Reaction of **1** with molecular iodine led to isomeric diiodo-derivatives **30** in a moderate yield (Scheme 10).



Scheme 10.

The lithiocyclopropene **18** formed from tribromide **13** and an excess of MeLi was also successfully trapped using a series of electrophiles E^+–X^- and carbonyl compounds $R^1R^2C{=}O$[26,34] (Scheme 11).



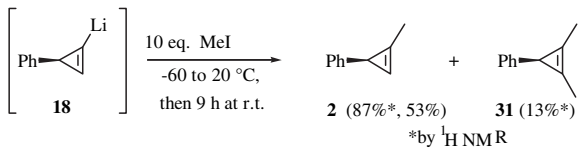
E-X: H_2O (MeOH), MeI;
$R^1R^2C{=}O$: $Me_2C{=}O$.

E = H, **1** (35*);
Me, **2** (87*);
$CMe_2(OH)$, **3** (73*).

* by ^{1}H NMR spectroscopy

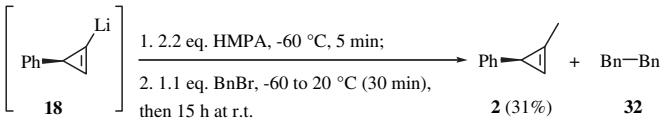
Scheme 11.

The reaction of **18** with MeI led to the formation of product **2**, accompanied by 1,2-bis-substituted side product **31**; the formation of this can be explained in terms of the further lithiation of **2** by the excess of MeLi (~20%) or due to the reaction between **18** and **2** (Scheme 12). The quantitative transformation of tribromide **13** to intermediate **18** is confirmed by the high overall yield of products **2** (87%) and **31** (13%).



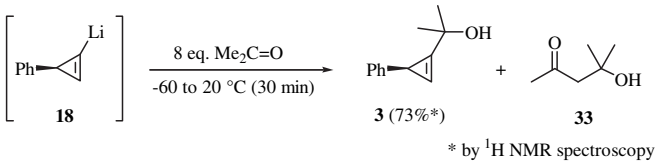
Scheme 12.

The reaction between **18** and benzyl bromide even in the presence of HMPA led to the formation of cyclopropene **2** in a satisfactory yield and dibenzyl **32** instead of the expected 1-benzyl derivative (Scheme 13). The methylated cyclopropene **2** is presumably derived by alkylation of **18** with methyl bromide generated under the reaction conditions used to form it.



Scheme 13.

Addition of **18** to the carbonyl group of acetone (Scheme 14) gave an almost equimolar mixture of carbinol **3** (73%) and 4-methyl-4-hydroxypentane-2-one **33** (71% counting on starting **13**). Unfortunately this mixture was not separated either by chromatography or by distillation. Attempts to obtain a similar result in the reactions of carbanion **18** with benzaldehyde, carbon dioxide and methyl chloroformate failed, with no clear products identified in each case.



Scheme 14.

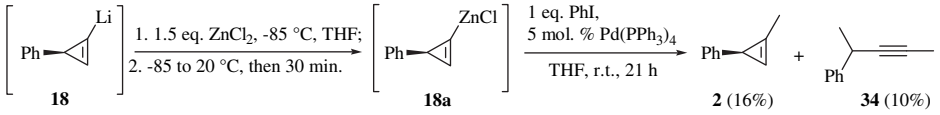
Formation of an equimolar ratio of compounds **3** and **33** along with the absence of 3-phenylcyclopropene **1** among the reaction products means that diacetone alcohol **33** derives from the aldol condensation of acetone, which enolises under the influence of the lithium alkoxide of carbinol **3** formed after the addition of **18** to the C=O bond, but not under the influence of lithiocyclopropene **18**.

Transformation of lithium carbanions of cyclopropenes into organozinc or tin compounds and their further cross-coupling with aryl- or vinylhalides in the presence of Pd(0) appeared to be effective for the synthesis of 1-aryl- and 1-vinylcyclopropenes.[14,35] However, attempts to apply this approach for the synthesis of 1,3-diphenylcyclopropene starting from intermediate **18** afforded only cyclopropene **2** together with acetylene **34**, both in low yields (Scheme 15)—again the methyl group presumably being introduced from methyl bromide formed in the generation of **18**.

Density functional theory (DFT) calculations using the M06/6-311+G** method suggest that 3-phenylcyclopropene **1**, like the 3-methyl-3-phenyl system **23**, has a preferred bisected conformation. In this conformation the HOMO for both species is localized on the aromatic ring and the cyclopropene single bonds, with the LUMO primarily localized to the cyclopropene carbon-hydrogen bonds (Fig. 1). There is a slight difference, however, in the relative vertical ionization potentials, which are calculated as 8.37 eV for the 3-phenylcyclopropene (−7.77 eV) and 8.30 eV for the 3-methyl-3-phenyl system (−7.65 eV).[31a] This predicts that, in this conformation, the 3-methyl-3-phenyl system should be very slightly more reactive and that, for both molecules, secondary orbital interactions with the aromatic ring could play a significant role.

The rotation barrier for cyclopropene **1** is calculated to be 14.0 kJ mol^{-1}, whereas that for the 3-methyl-3-phenyl system **23** is lower at 7.6 kJ mol^{-1}. These values correspond reasonably well with those previously calculated with the B3LYP/6-31G* method (13.7 and 5.6 kJ mol^{-1}, respectively).[24] This probably reflects the lower stability of the bisected geometry caused by the introduction of the methyl group. In support of this, calculations for 3-*tert*-butyl-3-phenylcyclopropene suggested a preferred geometry in which the plane of the benzene ring is parallel to the cyclopropene π-bond,[31a] indicating that steric factors could provide a major driver for the accessibility of specific conformers.

The non-bisected conformation exhibits differences in the HOMO and LUMO orbital coefficients from those for the bisected conformers (Fig. 2). Here the π-orbitals of the double bond become more important and are more pronounced for 3-methyl-3-phenyl-



Scheme 15.

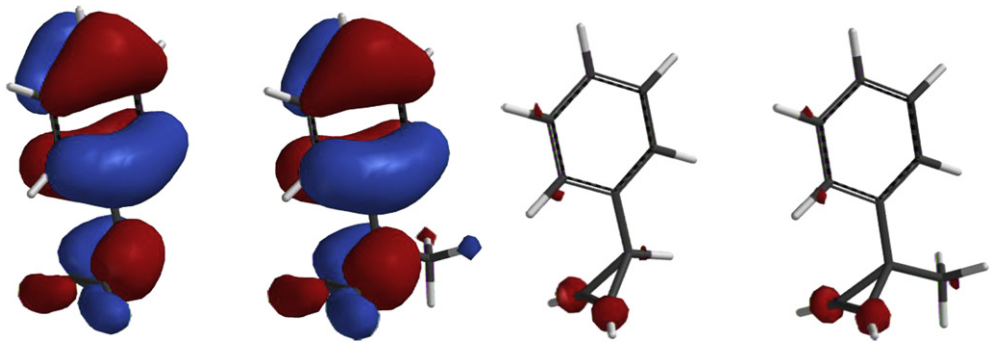


Figure 1. HOMOs (left) and LUMOs (right) for the preferred conformations of 3-phenylcyclopropene **1** and 3-methyl-3-phenylcyclopropene **23**.

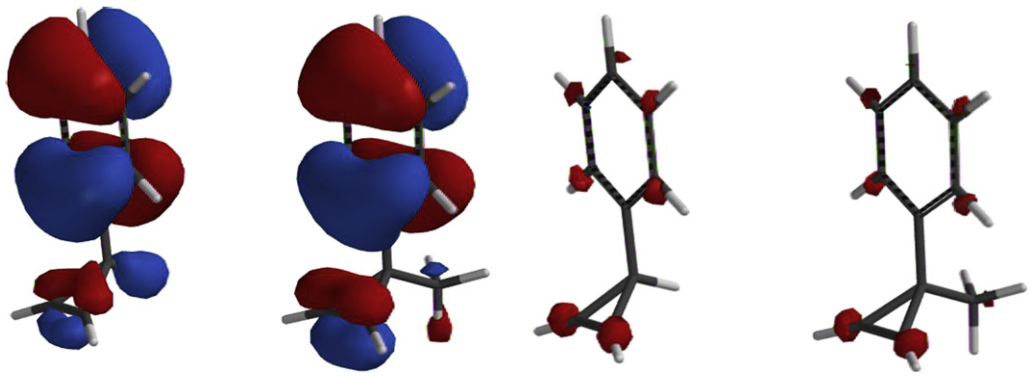


Figure 2. HOMOs (left) and LUMOs (right) of 3-phenylcyclopropene **1** and 3-methyl-3-phenylcycloprrpene in the unfavoured conformation.

cyclopropene. This is reflected by very different ionization potentials, which are 9.03 eV for the 3-phenylcyclopropene **1** and 8.63 eV for the 3-methyl-3-phenylcyclopropene **23**. This would predict a substantial difference in reactivity in this conformer, along with the improved accessibility in the 3-methyl-3-phenylcyclopropene for addition in which the phenyl group is *syn*- (Scheme 8). Here it is also likely that the phenyl group can participate in secondary orbital interactions. For 3-phenylcyclopropene **1**, the hydrogen on C-3 of the cyclopropene could provide a secondary bonding interaction. Thus the relative product formation could be explained by a combination of steric factors, preferring hydrogen *endo*- to the diene, however for 3-methyl-3-phenylcyclopropene **23**, the methyl group is both unable to manoeuver to avoid steric interactions, nor able to provide any compensating secondary bonding effect.

3. Conclusion

In summary, 3-phenylcyclopropene **1** and some 1-substituted derivatives are readily available and can be trapped in a range of reactions with a high degree of stereocontrol.

4. Experimental

4.1. General information

Commercial reagents were used without further purification unless stated. Diethyl ether and THF were distilled over sodium wire. Petroleum was of boiling point 40–60 °C. Reactions requiring anhydrous conditions were performed using oven dried glassware (250 °C) that was cooled under either dry nitrogen or argon; experiments were conducted under a positive atmosphere of argon. Unless stated, organic solutions were dried over anhydrous magnesium sulfate and evaporated at 14 mmHg; yields quoted are for purified compounds and any ratios given are calculated by comparing integrals in the ^{1}H NMR spectrum or by GLC data.

New compounds were homogenous by GLC or TLC. GLC was conducted using a Carlo Erba HRGC 5300 F.I.D. on a capillary column (30 m×0.32 mm id Phase, DB5 split ratio of 50:1) with nitrogen carrier gas. TLC was performed using Aldrich silica plates coated with silica gel 60 (F254). Column chromatography was conducted with Matrex Silica 60 (Fisher Scientific Int. Co.) under medium pressure. Melting points are uncorrected. Unless stated, infrared spectra were obtained as solutions in $CHCl_3$ or as liquid films on a Perkin Elmer 1600 FTIR spectrometer. Low resolution mass spectra were measured using a Finnigan 8430 spectrometer using EI 70 eV unless stated. Accurate mass measurements refer to ^{79}Br isotopes unless stated and were carried out on a Micromass™ GCT spectrometer. Microanalyses were performed on a Carlo Erba Model 1106 CHN analyzer. NMR spectra were recorded in $CDCl_3$, using Bruker AC250 or A500 spectrometers at 250 MHz or 500 MHz (^{1}H) and 62.9 MHz or 125 MHz (^{13}C). ^{13}C spectra were broad-band decoupled and in most cases corresponding DEPT spectra were also recorded. The results of DEPT spectra are quoted in the form of signs+(corresponding to CH and CH_3 groups) and -(corresponding to CH_2 groups), signals, which appear with no sign correspond to quaternary carbons. All previously described compounds were characterized by IR, ^{1}H and ^{13}C NMR and gave data identical to those in the literature.

4.2. 1,8,9-Triphenyl-12-oxatetracyclo[6.3.1.0^{2,7}.0^{9,11}]dodeca-2,4,6-triene (7)

1-Bromo-2-phenylcyclopropane **6** (500 mg, 2.54 mmol) in dry THF (2 mL) was added dropwise to a mixture of potassium *tert*-butoxide (342 mg, 3.04 mmol, 1.2 mol equiv) and 1,3-DPIBF (822 mg, 3.04 mmol, 1.2 mol equiv) in dry THF (10 mL) at rt over 3 min. The mixture was stirred for 3 h at rt, quenched with water (5 mL) and diluted with ether (10 mL). The organic layer was separated, the aqueous layer was extracted with ether (3×10 mL). The combined organic layers were washed with water (5 mL), dried and evaporated to give very viscous yellow oil (1.319 g), which was dissolved in dry THF (3 mL) and added to a mixture of maleic anhydride (301 mg, 3.04 mmol) and Et_3N (1.02 g, 10.03 mmol) in dry ether–THF mixture (1:1, 7 mL). The mixture was stirred for 30 min at rt, quenched with water (5 mL) and diluted with ether (10 mL). The organic layer was separated, the aqueous layer was extracted with ether (10 mL). The combined organic layers were extracted with 8% aq NaOH (3×15 mL), washed with brine (10 mL), dried and evaporated. Chromatography of the residue (769 mg) on silica (petrol–ether, 5:1, R_f 0.51) afforded adduct **7** (754 mg, 1.95 mmol, 77%) as small greenish crystals, mp 117–118 °C (MeOH) (Found: C 90.0, H 5.6%. $C_{29}H_{22}O$ requires: C 90.12, H 5.74%), which showed δ_H: 1.52 (1H, dd, *J*=6.7, 4.9 Hz, H-10), 2.04 (1H, dd, *J*=6.7, 3.7 Hz, H-11), 2.44 (1H, dd, *J*=4.9, 3.7 Hz, H-10), 6.66 (2H, m, Ar), 7.08–7.58 (15H, m, Ar), 7.74 (2H, m, Ar); δ_C: 21.6–, 33.8+, 41.2, 88.1, 90.5, 119.7+, 122.0+, 125.7+, 126.4+, 126.7+, 127.6+, 127.6+, 128.0+, 128.1+, 128.4+, 128.5+, 130.6+, 135.7, 136.6, 138.6, 148.1, 151.2; ν_{max} ($CHCl_3$): 3060 m, 3030 m, 1953 w, 1890 w, 1811 w, 1603 m, 1498 s, 1456 s, 1447 s, 1428 w, 1359 w, 1344 m, 1325 w, 1302 s, 1273 w, 1217 m, 1179 w, 1156 w, 1096 w, 1059 w, 1019 s, 979 s, 954 m, 918 m, 891 m, 864 w, 762 s, 700 s, 667 m, 648 m, 634 m cm^{-1}.

4.3. *trans*-Cinnamaldehyde diethylacetal (9)

To a solution of *trans*-cinnamaldehyde **8** (19.1 mL, 20.0 g, 151 mmol) and triethyl orthoformate (37.7 mL, 33.57 g, 227 mmol, 1.5 mol equiv) in absolute ethanol (150 mL) *N*-bromosuccinimide (269 mg, 1.51 mmol, 1.0 mol %) was added. The reaction mixture was stirred for 30 min at rt and poured into 10% cold aq NaOH (400 mL). The product was extracted with ether (3×120 mL). The combined organic layers were washed with water (3×50 mL), dried over K_2CO_3 and evaporated. Distillation gave diethylacetal **9**[36] (30.3 g, 147 mmol, 97%, t_R 5.03 min) as a colourless oil, bp 102–103 °C at 2 mmHg, which showed δ_H: 1.28 (6H, pseudo t, *J*=7.3, 7.0 Hz, 2×CH_3), 3.59 (2H, dq, *J*=14.4, 7.0 Hz, OCH_2), 3.70 (2H, dq, *J*=14.4, 7.3 Hz, OCH_2), 5.09 (1H, d, *J*=5.2 Hz, OCHO), 6.23 (1H, dd, *J*=16.2, 5.2 Hz, =CH), 6.70 (1H, d, *J*=16.2 Hz, =CHPh), 7.24–7.45 (5H, m, Ph); δ_C: 15.3+, 61.1–, 101.5+, 126.7+, 126.7+, 128.0+, 128.5+, 133.0+, 136.2; ν_{max}: 3082 w, 3059 w, 3026 m, 2975 s, 2928 s, 2877 s, 1949 w, 1655 m, 1600 m, 1578 m, 1495 m, 1449 m, 1372 m, 1338 m, 1298 m, 1267 m, 1202 w, 1138 s, 1052 s, 998 s, 969 s, 911 w, 836 m, 750 s, 693 s cm^{-1}.

4.4. *trans*-2,2-Dibromo-3-phenylcyclopropylcarbaldehyde diethylacetal (10)

Diethylacetal **9** (29.49 g, 143 mmol) was added to a mixture of bromoform (25 mL, 286 mmol, 2 mol equiv), dichloromethane (45 mL) and *n*-hexadecyltrimethylammonium bromide (2.61 g, 5 mol %). The mixture was stirred vigorously and sodium hydroxide (57.2 g, 1.43 mol) in water (58 mL) was added slowly at below 35 °C. After 6 h at 20 °C water (200 mL) was added and the mixture was extracted with dichloromethane (3×100 mL). The combined organic layers were washed with water (100 mL) and solvent was removed. The residue was dissolved in petrol–ether mixture (1:1, 500 mL) and filtered through Al_2O_3. Removal of the solvent and unreacted bromoform at 30–40 °C and 0.5 mmHg gave a residue, which was diethylacetal **10**[37] (46.84 g, 124 mmol, 87%, t_R 7.08 min) as dark red oil and showed δ_H: 1.21 (3H, t, *J*=7.0 Hz, CH_3), 1.34 (3H, t, *J*=7.0 Hz, CH_3), 2.32 (1H, pseudo t, *J*=8.5, 6.1 Hz, H-1), 2.88 (1H, d, *J*=8.5 Hz, H-3), 3.64–3.81 (4H, m, 2×OCH_2), 4.59 (1H, d, *J*=6.1 Hz, OCHO), 7.28–7.47 (5H, m, Ph); δ_C: 15.3+, 15.4+, 32.2, 37.0+, 38.8+, 61.5–, 61.6–, 103.4+, 127.7+, 128.4+, 128.8+, 135.4; ν_{max}: 3087 w, 3061 w, 3029 m, 2975 s, 2927 s, 2880 s, 1948 w, 1878 w, 1679 m, 1626 w, 1602 w, 1498

m, 1479 w, 1448 m, 1420 m, 1391 m, 1370 m, 1340 m, 1218 m, 1118 s, 1083 s, 1059 s, 952 w, 915 w, 878 w, 832 m, 757 m, 696 s cm^{-1}.

4.5. *trans*-2,2-Dibromo-3-phenylcyclopropane-carbaldehyde (11)

10% aq HCl (40 mL) was added to a solution of compound **10** (33.92 g, 89.7 mmol) in acetone (150 mL). The reaction mixture was stirred for 20 h at rt, then concentrated at reduced pressure. The product was extracted with ether (2×100 mL), the combined organic layers were washed with water (2×50 mL) and dried. Solvent was removed in vacuo to afford aldehyde **11**[38] (26.33 g, 86.6 mmol, 96%) as brown oil, which showed δ_H: 2.90 (1H, dd, J=8.2, 4.6 Hz, H-1), 3.56 (1H, d, J=8.2 Hz, H-3), 7.28–7.39 (5H, m, Ph), 9.46 (1H, d, J=4.6 Hz, CHO); ν_{max}: 3060 w, 3031 w, 2977 w, 2927 w, 2846 w, 2737 w, 1951 w, 1880 w, 1712 s, 1675 m, 1625 w, 1604 w, 1497 m, 1449 m, 1386 m, 1332 w, 1280 w, 1168 m, 1129 s, 1082 m, 1049 m, 1029 m, 1009 m, 977 m, 930 w, 803 w, 757 m, 731 m, 695 s cm^{-1}.

4.6. *trans*-2,2-Dibromo-3-phenylcyclopropane carboxylic acid (12)

Jones' reagent (30 mL, 80 mmol) was added in 1 mL portions to a stirred solution of aldehyde **11** (25.48 g, 83.8 mmol) in acetone (250 mL) at −2 to 3 °C for 30 min. The mixture was stirred at −5 °C for 30 min, then carefully poured in cold water (200 mL) and extracted with ether (3×100 mL). The combined organic layers were washed with water (3×50 mL) and extracted with 5% aq $NaHCO_3$ (3×70 mL), followed by acidification with cold 10% HCl and subsequent extraction with ether (2×100 mL). The organic phases were washed with brine (20 mL), dried and evaporated to give crude product (19.0 g), which was further recrystallized from benzene–hexane (1:1, 100 mL) to give acid **12**[39] (16.28 g, 51 mmol, 61%) as white powder, mp 144–145 °C (Found: C 37.8, H 2.6%. $C_{10}H_8Br_2O_2$ requires: C 37.54, H 2.52%), which showed δ_H: 2.81 (1H, d, J=7.8 Hz, H-1), 3.34 (1H, d, J=7.8 Hz, H-3), 7.15–7.32 (5H, m, Ph); δ_C: 28.3, 37.0+, 41.5+, 128.3+, 128.6+, 128.7+, 133.7, 172.4; ν_{max} ($CHCl_3$): 3200–2200 br s, 3060 m, 2591 m, 1950 w, 1708 s, 1603 w, 1496 w, 1442 s, 1311 m, 1170 m, 1082 w, 950 m, 899 m, 862 m, 702 s, 690 s cm^{-1}.

4.7. *cis*/*trans*-1,1,2-Tribromo-3-phenylcyclopropane (13)

Bromine (0.67 mL, 2.1 g, 13.0 mmol, 1.05 mol equiv) in dry CH_2Cl_2 (50 mL) was added dropwise to a solution of acid **12** (3.96 g, 12.36 mmol) and red mercury(II) oxide (2.01 g, 9.28 mmol, 0.75 mol equiv) in dry CH_2Cl_2 (50 mL) under Ar atmosphere at 0 °C over 10 min. After 5 h of stirring at 0 °C the mixture was filtered through a glass filter and the residue was washed with dichloromethane (50 mL) and hexane (3×70 mL). The organics were concentrated in vacuo, diluted with hexane (10 mL) and filtered through a pad of silica (hexane, 3×70 mL). The solvent was removed to give tribromide **13** (3.73 g, 10.5 mmol, 85%, mixture of isomers, *t*:*c*=5:1) as a colourless oil (Found M^+: 353.8076. $C_9H_7{}^{79}Br_2{}^{81}Br$ requires: 353.8077). The *trans*-isomer showed δ_H: 2.99 (1H, d, J=7.0 Hz, H-2), 3.88 (1H, d, J=7.0 Hz, H-3), 7.26–7.41 (5H, m, Ph); δ_C: 33.2+, 33.7, 45.3+, 128.3+, 128.5+, 128.6+, 134.0; *cis*-isomer showed δ_H: 3.04 (1H, d, J=9.8 Hz, H-2), 4.11 (1H, d, J=9.8 Hz, H-3), 7.26–7.55 (5H, m, Ph); δ_C: 31.6, 36.7+, 37.7+, 128.0+, 128.2+, 130.2+, 132.6. The mixture showed ν_{max}: 3038 s, 1948 w, 1800 w, 1602 m, 1584 w, 1496 s, 1447 s, 1224 m, 1176 m, 1106 w, 1081 m, 1044 s, 1028 m, 1002 w, 913 w, 830 s, 787 m, 738 s, 690 s cm^{-1}; *m*/*z*, %: 357 (M^+, ^{81}Br+^{81}Br+^{81}Br–H, 0.5), 355 (M^+, ^{79}Br+^{81}Br+^{81}Br–H, 1.3), 353 (M^+, ^{79}Br+^{79}Br+^{81}Br–H, 1.3), 351 (M^+, ^{79}Br+^{79}Br+^{79}Br–H, 0.5), 275 (3), 273 (5), 271 (2), 195 (21), 193 (19), 115 (4), 88 (5), 86 (79), 84 (100); R_f 0.56 (petrol–ether, 5:1).

4.8. 1-Bromo-3-phenylcyclopropene (4), 3-bromo-3-phenylpropyne (14) and 1-bromo-3-phenyl-propadiene-1,2 (15)

Methyllithium in ether (0.72 mL, 0.93 mmol, 1.30 M, 1.1 mol-equiv) was added dropwise to tribromide **13** (300 mg, 0.84 mmol) in dry ether (10 mL) at −82 to −80 °C over 2 min. The mixture was stirred for 20 min at −80 °C, allowed to reach −40 °C (10 min) and quenched with water (1 mL). The organic layer was separated, the aqueous layer was extracted with ether (5 mL). The combined organic layers were washed with brine (2 mL), dried and evaporated to give an orange oil (153 mg), which by ^{1}H NMR spectroscopy contained 50% of cyclopropene **4**, which showed δ_H: 3.20 (1H, s, H-3), 7.14–7.43 (6H, m, H-2, Ph) together with acetylene **14**[40] (34%) and allene **15**[41] (16%). After 15 h at rt the neat sample was chromatographed on silica (pentane–ether, 15:1, R_f 0.47) to yield a mixture of **14** and **15** (127 mg, 0.65 mmol, 77%, ratio **14**/**15**=1.0:0.3 (by ^{1}H NMR), compounds not separated) as a colourless oil. Compound **14** showed δ_H: 2.95 (1H, d, J=2.5 Hz, H-1), 5.71 (1H, d, J=2.5 Hz, H-3), 7.36–7.41 (3H, m, Ph), 7.58 (2H, m, Ph); δ_C: 35.6+, 77.7+, 102.6, 127.7+, 128.9+, 129.1+, 138.4. Compound **15** showed δ_H: 6.33 (1H, d, J=6.0 Hz, =CH), 6.37 (1H, d, J=6.0 Hz, =CH), 7.35–7.41 (5H, m, Ph); δ_C: 74.8+, 81.0+, 202.9. The mixture showed ν_{max}: 3290 s, 3060 m, 3030 m, 2963 w, 2121 m, 1942 m, 1882 w, 1806 w, 1691 w, 1602 w, 1494 s, 1454 s, 1338 w, 1270 m, 1187 m, 1135 s, 1075 w, 986 m, 814 s, 764 s, 694 s cm^{-1}.

4.9. 9-Bromo-1,8,10-triphenyl-12-oxatetracyclo-[6.3.1.$0^{2,7}$.$0^{9,11}$]dodeca-2,4,6-triene (16)

Methyllithium in ether (0.72 mL, 0.93 mmol, 1.30 M, 1.1 mol equiv) was added dropwise to a mixture of tribromide **13** (300 mg, 0.84 mmol) and 1,3-DPIBF (251 mg, 0.93 mmol, 1 mol equiv) in dry ether (10 mL) at −72 to −70 °C over 2 min. The solution was stirred for 20 min at −70 °C and 20 min at 15 °C, then cooled to −45 °C and quenched with water (2 mL). The organic layer was separated, the aqueous layer was extracted with ether (3×5 mL). The combined organic layers were washed with brine (3 mL), dried and evaporated to give very viscous brown oil (426 mg). To remove the excess of 1,3-DPIBF, this material was dissolved in dry THF (2 mL) and added to a mixture of maleic anhydride (92 mg, 0.93 mmol) and Et_3N (310 mg, 3.07 mmol) in dry ether–THF mixture (1:1, 5 mL). The mixture was stirred for 35 min at rt, quenched with water (4 mL) and diluted with ether (10 mL). The organic layer was separated, the aqueous layer was extracted with ether (10 mL). The combined organic layers were extracted with 8% aq NaOH (4×10 mL), washed with brine (10 mL), dried and evaporated. Chromatography of the residue (398 mg) on silica (petrol–ether, 5:1, R_f 0.51) gave compound **16** (249 mg, 0.53 mmol, 64%) as a white powder, mp 157–159 °C (MeOH) (Found M^+: 464.0757. $C_{29}H_{21}{}^{79}BrO$ requires: 464.0776), which showed δ_H: 2.50 (1H, d, J=4.4 Hz, H-11), 3.85 (1H, d, J=4.4 Hz, H-10), 7.19 (1H, m, Ar), 7.25–7.55 (14H, m, Ar), 7.69 (2H, m, Ar), 7.85 (2H, m, Ar); δ_C: 37.3+, 38.4+, 50.9, 89.1, 92.4, 119.8+, 122.6+, 126.5+, 127.0+, 127.2+, 127.9+, 128.2+, 128.59+, 128.62+, 128.8+, 128.9+, 129.3+, 129.6+, 133.1, 135.1, 136.8, 147.7, 148.7; ν_{max} ($CHCl_3$): 3061 m, 3029 m, 1955 w, 1605 m, 1497 s, 1449 s, 1381 w, 1341 w, 1304 s, 1217 s, 1182 w, 1114 w, 1078 w, 1050 w, 981 s, 910 w, 749 s, 696 s cm^{-1}; *m*/*z* %: 466 (M^+, ^{81}Br, 0.05), 464 (M^+, ^{79}Br, 0.05), 387 (1), 386 (33), 385 (81), 307 (23), 280 (11), 279 (33), 278 (12), 203 (5), 202 (12), 167 (34), 106 (6), 105 (100), 77 (32).

4.10. 2-Bromo-3-*anti*-phenyltricyclo[3.2.1.$0^{2,4}$]octene-6 (17)

Methyllithium in ether (0.91 mL, 0.88 mmol, 0.97 M, 1.05 mol equiv) was added dropwise to tribromide **13** (300 mg, 0.84 mmol) in dry ether (10 mL) at −75 °C over 2 min. The solution was stirred for 20 min at −70 °C and then methanol (0.15 mL) was added followed

by subsequent addition of freshly distilled cyclopentadiene (0.35 mL, 280 mg, 4.2 mmol, 5 mol equiv). The resulting solution was allowed to reach rt, stirred for 2 h and quenched with water (2 mL). The organic layer was separated, the aqueous layer was extracted with ether (3 mL). The combined organics were washed with water (3 mL), dried and evaporated to give bromoadduct **17** (230 mg, purity ~90% by ^{1}H NMR spectroscopy) as a colourless oil, which showed δ_H: 1.84 (1H, d, J=7.3 Hz, H-bridge), 2.17 (1H, t, J=4.3 Hz, H-4), 2.31 (1H, d, J=4.3 Hz, H-3), 2.31 (1H, d, J=7.3 Hz, H-bridge), 3.19 (1H, s), 3.26 (1H, s), 5.95 (1H, t, J=8.9 Hz, =CH), 6.13 (1H, t, J=8.9 Hz, =CH), 7.14–7.30 (5H, m, Ph); δ_C: 27.4, 29.7, 41.2, 45.3, 55.7, 61.1, 126.5, 127.8, 128.9, 132.8, 134.3, 138.1; ν_{max}: 3070 m, 3025 m, 2990 s, 2940 s, 2878 m, 1960 w, 1880 w, 1600 m, 1570 w, 1500 m, 1452 m, 1380 w, 1330 m, 1280 w, 1253 m, 1240 m, 1160 m, 1120 w, 1105 w, 1090 m, 1073 m, 1027 m, 920 m, 883 m, 842 m, 795 m, 750 s, 710 s. The title compound was unstable when neat or as solution in $CDCl_3$ at 5–20 °C under Ar atmosphere and after 24 h formed a complex mixture of undefined products.

4.11. 3-Phenylcyclopropene (1)

Methyllithium in ether (1.42 mL, 1.85 mmol, 1.30 M, 2.2 mol equiv) was added dropwise to tribromide **13** (300 mg, 0.84 mmol) in dry ether (10 mL) at −82 to −80 °C over 3 min. The mixture was stirred for 5 min at −80 °C and allowed to reach rt (20 min). After a further 30 min at rt the resulting solution was cooled to −40 °C and carefully quenched by dropwise addition of water (2 mL). The organic layer was quickly decanted and concentrated at −20 °C. It gave a pale yellow oil (94 mg), which by integration contained by ^{1}H NMR spectroscopy approx. 35% of 3-phenylcyclopropene **1**, which showed δ_H: 2.70 (1H, s, H-3), 7.14–7.31 (7H, m, H-1,2; Ph); δ_C: 19.5+, 108.6+, 125.6+, 128.0+, 128.6+, 147.1; ν_{max}: 3104 w, 3059 w, 3025 m, 2938 m, 1646 s, 1601 s, 1491 s, 1451 s, 1354 w, 1277 w, 1072 w, 1025 m, 989 s, 909 w, 745 s, 698 s cm^{-1}. The other components of the mixture remained unidentified.

4.12. Preparation of an ethereal solution of 3-phenylcyclopropene (1)

Methyllithium in ether (1.42 mL, 1.85 mmol, 1.30 M, 2.2 mol equiv) was added dropwise to tribromide **13** (300 mg, 0.84 mmol) in dry ether (10 mL) at −82 to −80 °C over 3 min. After 5 min at −80 °C the mixture was allowed to reach rt (20 min), stirred for 30 min and then cooled down to: (**a**) −60 °C and carefully quenched by addition of methanol (0.15 mL) over 2 min. The resulting ethereal solution of **1** was directly used for [4+2]-reactions with 1,3-DPIBF, furan, isoprene and cyclopentadiene (see Experiments 4.12.1–4.12.4); (**b**) −40 °C and quenched with water (2 mL). The organic layer was separated, the aqueous layer was extracted with ether (5 mL). The combined organic layers were dried and concentrated to ca. ~5 mL (the whole work up sequence requires ~1 h). Thus produced, the ethereal solution of **1** was used immediately for [3+2]-reactions with diazomethane, benzonitrile oxide and ethyl diazoacetate (see Experiments 4.12.5–4.12.7) and for reaction with iodine (Section 4.12.8).

*4.12.1. 1,8,10-Triphenyl-12-oxatetracyclo[6.3.1.0^{2,7}.0^{9,11}]dodeca-2,4,6-triene (**19**).* 1,3-DPIBF (114 mg, 0.42 mmol, 1 mol equiv) in dry THF (1 mL) was added to an ethereal solution of **1** prepared from tribromide **13** (150 mg, 0.42 mmol) and methyllithium in ether (0.67 mL, 0.94 mmol, 1.40 M, 2.2 mol equiv) in dry ether (5 mL) according to procedure 4.12a. The resulting solution was allowed to reach rt (20 min) and stirred for 20 min, then cooled to 0 °C and quenched with water (2 mL). The organic layer was separated, the aqueous layer was extracted with ether (2×5 mL). The combined organic layers were washed with brine (3 mL), dried and evaporated to give a brown creamy residue (186 mg), which was recrystallized from MeOH (2 mL) to yield compound **19** (113 mg, 0.29 mmol, 70%) as a white powder, mp 156–158 °C (Found M$^+$: 386.1669. $C_{29}H_{22}O$ requires: 386.1671), which showed δ_H: 2.20 (2H, d, J=3.2 Hz, H-9,11), 3.30 (1H, t, J=3.2 Hz, H-10), 7.11–7.76 (19H, m, Ar); δ_C: 33.1+, 35.2+, 89.6, 119.5+, 126.1+, 126.3+, 126.4+, 128.3+, 128.40+, 128.43+, 128.6+, 136.1, 140.1, 150.2; ν_{max} ($CHCl_3$): 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 cm^{-1}; m/z, %: 387 (M$^+$+1, 2), 386 (M$^+$, 8), 368 (3), 291 (4), 282 (9), 281 (95), 280 (40), 279 (12), 265 (6), 252 (4), 204 (4), 203 (19), 202 (14), 165 (4), 138 (3), 106 (6), 105 (100), 77 (14), 51 (2); R_f 0.50, (petrol–ether, 1:1).

*4.12.2. anti-3-Phenyl-8-oxatricyclo[3.2.1.0^{2,4}]oct-6-ene (**20**).* Freshly distilled furan (2.0 mL, 1.87 g, 27.5 mmol, 33 mol equiv) was added dropwise to an ethereal solution of **1** prepared according to procedure 4.12a. The resulting mixture was stirred for 24 h at rt and quenched with water (4 mL). The organic layer was separated, the aqueous layer was extracted with ether (2×5 mL). The combined organic layers were washed with water (5 mL), dried and evaporated. The crude product (158 mg) was purified on silica (petrol–ether, 20:1 to 5:1) to yield *exo*-**20** (97 mg, 0.53 mmol, 63%, R_f 0.31 (petrol–ether, 20:1)) as yellowish crystals, mp 98–99 °C (Found M$^+$: 184.0888. $C_{13}H_{12}O$ requires: 184.0888) and *endo*-**20** (22 mg, 0.12 mmol, 14%, R_f 0.15 (petrol–ether, 5:1)) as a yellowish viscous mass (Found M$^+$: 184.0882. $C_{13}H_{12}O$ requires: 184.0888). *exo*-**20** showed δ_H: 1.53 (2H, d, J=3.2 Hz, H-2,4), 3.00 (1H, t, J=3.2 Hz, H-3), 4.92 (2H, s, H-1,5), 6.58 (2H, s, H-6,7), 7.10–7.29 (5H, m, Ph); δ_C: 30.3+, 35.4+, 77.8+, 125.9+, 126.2+, 128.3+, 137.7+, 140.6; ν_{max} ($CHCl_3$): 3079 w, 2991 s, 1604 m, 1495 m, 1454 s, 1298 s, 1261 w, 1236 m, 1152 m, 1095 w, 1069 m, 1056 s, 1010 s, 980 w, 916 s, 902 s, 865 s, 832 w, 786 w, 750 s, 712 m, 699 s, 650 m cm^{-1}; m/z, %: 185 (M$^+$+1, 3), 184 (M$^+$, 17), 183 (M$^+$−1, 20), 168 (7), 167 (14), 166 (10), 165 (21), 156 (33), 155 (100), 154 (26), 153 (46), 152 (26), 142 (9), 141 (35), 130 (6), 129 (35), 128 (54), 127 (20), 116 (11), 115 (65), 105 (10), 102 (12), 91 (67), 89 (14), 78 (37), 77 (48), 63 (17), 51 (28). *endo*-**20** showed δ_H: 2.11 (1H, t, J=2.8 Hz, H-3), 2.20 (2H, d, J=2.8 Hz, H-2,4), 5.09 (2H, s, H-1,5), 6.22 (2H, s, H-6,7), 7.05–7.29 (5H, m, Ph); δ_C: 25.6+, 41.1+, 79.4+, 126.2+, 126.4+, 128.3+, 131.0+, 139.6; ν_{max} ($CHCl_3$): 3029 m, 3005 m, 1600 m, 1500 m, 1454 m, 1382 w, 1313 s, 1274 w, 1176 w, 1147 w, 1071 w, 1053 w, 1032 w, 989 s, 947 w, 914 s, 878 s, 856 s, 828 m, 741 s, 703 s, 697 s, 614 s cm^{-1}; m/z, %: 185 (M$^+$+1, 0.6), 184 (M$^+$, 3), 183 (M$^+$−1, 1.3), 168 (2), 167 (3), 165 (3), 156 (5), 155 (6), 141 (5), 128 (5), 115 (5), 91 (6), 88 (9), 86 (61), 84 (100), 77 (4), 51 (28).

*4.12.3. 3-Methyl-exo-7-phenylbicyclo[4.1.0]hept-3-ene (**21**).* Freshly distilled isoprene (1.0 mL, 681 mg, 10.0 mmol, 12 mol equiv) was added dropwise to an ethereal solution of **1** prepared according to procedure 4.12a. The resulting mixture was stirred for 53 h at rt and quenched with water (3 mL). The organic layer was separated, the aqueous layer was extracted with ether (2×5 mL). The combined organic layers were washed with brine (3 mL), dried and evaporated. The crude product was chromatographed on silica (pentane, R_f 0.47) to give pure adduct **21** (126 mg, 0.68 mmol, 81%) as a colourless oil (Found M$^+$: 184.1258. $C_{14}H_{16}$ requires: 184.1252), which showed δ_H: 1.42 (1H, ddd, J=4.7, 9.1, 9.5 Hz), 1.48 (1H, ddd, J=4.4, 8.8, 9.1 Hz), 1.72 (3H, s, CH_3), 1.79 (1H, pseudo t, J=4.4, 4.7 Hz, H-7), 2.32 (1H, d, J=18.0 Hz), 2.41–2.56 (3H, m), 5.31 (1H, m, =CH), 7.07–7.31 (5H, m, Ph); δ_C: 21.6+, 22.7+, 24.09+, 24.13–, 24.9+, 28.4–, 117.4+, 124.9+, 125.3+, 128.2+, 130.1, 144.2; ν_{max}: 3084 w, 3059 w, 3010 s, 2964 s, 2873 s, 2831 s, 1936 w, 1676 w, 1601 s, 1580 w, 1500 s, 1437 m, 1377 w, 1261 w, 1220 m, 1154 w, 1080 w, 1057 w, 1032 m, 999 w, 924 w, 806 m, 739 s, 696 s cm^{-1}; m/z, %: 185 (M$^+$+1, 7), 184 (M$^+$, 100), 169 (41), 165 (17), 156 (8), 155 (37), 154 (29), 153 (22), 152

(17), 149 (21), 143 (13), 142 (18), 141 (63), 129 (57), 128 (84), 127 (16), 119 (10), 116 (19), 115 (77).

*4.12.4. anti-3-Phenyltricyclo[3.2.1.0^{2,4}]oct-6-ene (**22**).* Freshly distilled cyclopentadiene (0.35 mL, 280 mg, 4.2 mmol, 5 mol equiv) was added dropwise to an ethereal solution of **1** prepared from tribromide **13** (300 mg, 0.84 mmol) and methyllithium in ether (2.0 mL, 1.85 mmol, 0.92 M, 2.2 mol equiv) in dry ether (10 mL) according to procedure 4.12a. The resulting mixture was stirred for 1 h at rt and quenched with water (2 mL). The organic layer was separated, the aqueous layer was extracted with ether (3 mL). The combined organics were washed with water (3 mL), dried and evaporated to yield an orange oil (140 mg), which contained adduct **22** (purity>90% by ^{1}H NMR spectroscopy). This crude product was purified on silica (petrol, R_f 0.53) to give compound **22** (98 mg, 0.54 mmol, 64%) as colourless oil (Found: C 92.3, H 7.8%. $C_{14}H_{14}$ requires: C 92.26, H 7.74%), which showed δ_H: 1.68 (3H, br s, H-2,3,4), 1.68 (1H, d, J=6.7 Hz, H-bridge), 1.80 (1H, d, J=6.7 Hz, H-bridge), 2.98 (2H, s, H-1,5), 5.87 (2H, s, H-6,7), 7.00–7.21 (5H, m, Ph); δ_C: 23.9+, 34.3+, 43.6+, 63.3–, 125.4+, 126.3+, 128.0+, 131.4+, 142.1; ν_{max}: 3135 w, 3090 m, 3065 m, 3035 m, 2980 s, 2937 m, 2870 m, 1600 m, 1502 m, 1457 m, 1380 w, 1340 m, 1255 m, 1240 m, 1215 w, 1180 m, 1120 w, 1080 w, 1055 m, 1033 m, 970 w, 919 w, 907 w, 890 m, 830 w, 800 w, 750 s, 710 s cm^{-1}.

*4.12.5. exo-6-Phenyl-2,3-diazabicyclo[3.1.0]hex-2-ene (**26**).* Diazomethane in ether (7 mL, ~1.2 mmol, ~0.2 M, 1.4 mol equiv) was added dropwise to an ethereal solution of **1** prepared according to procedure 4.12b at 0 °C over 10 min. The yellow-green reaction mixture was stirred for 50 min at 0 °C and the solvent was removed under reduced pressure. The crude product was columned on silica (pentane–ether, 1:1, R_f 0.36) to afford adduct **26** (82 mg, 0.52 mmol, 62%) as a yellowish powder, mp 59–61 °C (Found M$^+$: 158.0851. $C_{10}H_{10}{}^{14}N_2$ requires: 158.0844), which showed δ_H: 1.20 (1H, dd, J=1.6, 4.4 Hz, H-6), 2.15 (1H, dddd, J=1.3, 4.4, 4.7, 6.6 Hz, H-5), 4.54 (1H, dd, J=1.3, 19.2 Hz, H-4), 4.74 (1H, dd, J=6.6, 19.2 Hz, H-4), 4.93 (1H, dd, J=1.6, 4.7 Hz, H-1), 7.07 (2H, m, Ph), 7.25–7.35 (3H, m, Ph); δ_C: 23.6+, 32.5+, 73.2+, 80.1–, 126.0+, 126.8+, 128.6+, 138.3; ν_{max} ($CHCl_3$): 3055 m, 2925 m, 1955 w, 1835 w, 1604 s, 1516 s, 1496 s, 1455 s, 1415 s, 1386 m, 1285 m, 1268 m, 1176 m, 1146 m, 1070 s, 1037 m, 990 m, 931 m, 914 m, 884 m, 751 s, 698 s cm^{-1}; m/z (CI, CH_4), %: 158 (M$^+$, 8), 157 (M$^+$−H, 100), 156 (11), 139 (5), 137 (5), 125 (3), 123 (5), 111 (1), 109 (3), 107 (2), 97 (2), 95 (1).

*4.12.6. exo-4,6-Diphenyl-2-oxo-3-azabicyclo[3.1.0]hex-3-ene (**27**).* A solution of Et_3N (78 mg, 0.77 mmol, 0.9 mol equiv) in dry ether (1 mL) was added dropwise to a stirred ethereal solution of **1** (method 4.12b) and benzohydroximinoyl chloride (120 mg, 0.77 mmol, 0.9 mol equiv) in dry ether (2 mL) at −15 °C over 1 min. The mixture was stirred for 30 min at −15 °C and 7 h at rt, carefully quenched with 1 M HCl (4 mL), diluted with water (5 mL) and ether (5 mL). The organic layer was separated and the aqueous layer was extracted with ether (2×5 mL). The combined organics were washed with water (2×5 mL), dried and evaporated. Chromatography of the residue (164 mg) on silica (petrol–ether, 5:1 to CH_2Cl_2, R_f 0.42) gave compound **27** (141 mg, 0.60 mmol, 78%) as a white powder, mp 154–157 °C (dec) (Found M$^+$: 235.1006. $C_{16}H_{13}{}^{14}NO$ requires: 235.0997), which showed δ_H: 1.85 (1H, dd, J=1.9, 3.2 Hz, H-6), 3.24 (1H, dd, J=3.2, 5.4 Hz, H-5), 5.11 (1H, dd, J=1.9, 5.4 Hz, H-1), 7.05 (2H, m, Ph), 7.28–7.48 (6H, m, Ph), 7.84 (2H, m, Ph); δ_C: 23.7+, 35.6+, 70.8+, 125.6+, 126.5+, 127.3+, 128.6, 128.7+, 128.8+, 130.5+, 138.3, 161.6; ν_{max} ($CHCl_3$): 3087 w, 3060 m, 3043 s, 1958 w, 1891 w, 1602 s, 1582 w, 1544 m, 1496 s, 1448 s, 1382 s, 1362 s, 1286 w, 1156 w, 1076 m, 1052 m, 1031 m, 1006 s, 973 m, 922 m, 898 m, 866 s, 847 m, 696 s cm^{-1}; m/z, %: 236 (M$^+$+1, 1), 235 (M$^+$, 8), 234 (M$^+$−1, 10), 219 (30), 206 (26), 132 (9), 131 (23), 115 (6), 104 (17), 103 (40), 85 (55), 84 (100), 77 (17), 51 (9).

*4.12.7. Ethyl 5-phenyl-2,5-dihydropyridazine-3-carboxylate (**29**).* Ethyl diazoacetate (0.1 mL, 96 mg, 0.84 mmol, 1 mol equiv) in ether (2 mL) was added dropwise to a stirred ethereal solution of **1** (method 4.12b) at 0 °C. After 20 h at rt solvent was removed under reduced pressure. The crude product was purified on silica (petrol–ether, 5:4, R_f 0.41) to give ethyl ester **29** (38 mg, 0.17 mmol, 20%) as an orange oil (Found M$^+$: 230.1085. $C_{13}H_{14}{}^{14}N_2O_2$ requires: 230.1055), which showed δ_H: 1.33 (3H, t, J=7.0 Hz, CH_3), 4.07 (1H, dd, J=4.3, 2.4 Hz, H-5), 4.28 (2H, q, J=7.0 Hz, OCH_2), 5.73 (1H, dd, J=4.3, 2.1 Hz, H-4), 6.56 (1H, dd, J=2.4, 2.1 Hz, H-6), 7.24–7.41 (5H, m, Ph), 7.83 (1H, br s, NH); δ_C: 14.1+, 39.8+, 61.6–, 105.4+, 127.4+, 127.9+, 129.0+, 129.8, 135.5+, 142.1, 162.0; ν_{max}: 3386 br s, 3061 w, 3029 w, 2982 m, 2937 w, 2905 w, 1717 s, 1678 s, 1654 s, 1600 m, 1493 m, 1454 s, 1394 m, 1371 s, 1320 m, 1301 s, 1264 s, 1210 s, 1132 s, 1096 m, 1027 m, 911 m, 864 m, 752 s, 733 s, 700 s cm^{-1}; m/z, %: 231 (M$^+$+1, 1), 230 (M$^+$, 8), 229 (M$^+$−1, 15), 211 (6), 201 (9), 184 (12), 183 (6), 157 (13), 156 (95), 155 (31), 153 (21), 131 (8), 130 (22), 129 (40), 128 (21), 115 (18), 102 (100), 77 (27).

*4.12.8. 1,2-Di-iodo-3-phenylcyclopropene (**30**).* A solution of iodine (235 mg, 0.92 mmol, 1.1 mol equiv) in $CHCl_3$ (8 mL) was added dropwise to an ethereal solution of **1** (method 4.12b) at rt. The mixture was stirred for 30 min at rt and quenched with satd aq $Na_2S_2O_3$ solution (5 mL). The organic layer was separated, the aqueous layer was extracted with chloroform (5 mL). The combined organic layers were washed with water (5 mL), dried and evaporated. It afforded di-iodide **30** (190 mg, 0.51 mmol, 61%, mixture of isomers, t:c=1:1 by ^{1}H NMR spectroscopy) as a brown oil (Found M$^+$: 369.8721. $C_9H_8I_2$ requires: 369.8716). The mixture showed δ_H: 2.30 (1H$_c$, t, J=5.7 Hz, H-3), 2.37 (1H$_t$, dd, J=8.7, 5.8 Hz, H-3), 3.07 (2H$_c$, d, J=5.7 Hz, H-1,2), 3.14 (1H$_t$, dd, J=5.8, 4.3 Hz), 3.31 (1H$_t$, dd, J=8.7, 4.3 Hz), 7.07–7.41 (5H, m, Ph); δ_C: −10.3+, 0.3+, 2.0+, 32.8+, 39.4+, 125.7+, 127.3+, 127.5+, 128.2+, 128.3+, 128.8+, 136.7, 138.2; ν_{max}: 3059 m, 3025 s, 2893 m, 1944 w, 1602 s, 1492 s, 1450 m, 1352 w, 1215 w, 1155 w, 1113 w, 1072 m, 1029 m, 989 m, 910 w, 839 w, 760 s, 747 s, 696 s, 634 s cm^{-1}; m/z, %: 370 (M$^+$, 0.05), 254 (5), 243 (M$^+$−I, 56), 128 (3), 127 (I$^+$, 100), 116 (2), 114 (3), 89 (39), 63 (12).

4.13. Preparation of an ethereal solution of 1-lithio-3-phenylcyclopropene (18) and its reactions with electrophiles

Methyllithium in ether (1.42 mL, 1.85 mmol, 1.30 M, 2.2 mol equiv) was added dropwise to tribromide **13** (300 mg, 0.84 mmol) in dry ether (10 mL) at −82 to −80 °C over 3 min. The mixture was stirred for 5 min at −80 °C and allowed to reach rt (20 min). After a further 30 min at rt the prepared solution of **18** was cooled down to −60 °C and directly used for reactions with electrophiles (MeI, BnBr, acetone, PhCHO, $ClCO_2Me$, CO_2, $ZnCl_2$).

*4.13.1. 1-Methyl-3-phenylcyclopropene (**2**) and 1,2-dimethyl-3-phenylcyclopropene (**31**).* Methyl iodide (0.5 mL, 1.14 g, 8.0 mmol, 9.5 mol equiv) was added dropwise to an ethereal solution of **18** at −60 °C. The mixture was allowed to reach rt, stirred for 9 h, cooled to −10 °C and quenched with water (2 mL). The organic layer was separated, the aqueous layer was extracted with ether (2×5 mL). The combined organic layers were washed with brine (3 mL), dried and evaporated. The crude product (112 mg, ratio, %: **2**/**31**=87:13 by ^{1}H NMR spectroscopy) was columned on silica (pentane, R_f 0.43) to give cyclopropene **2** (57 mg, 0.44 mmol, 53%) as colourless oil (Found M$^+$: 130.0787. $C_{10}H_{10}$ requires: 130.0783), which showed δ_H: 2.19 (3H, s, CH_3), 2.59 (1H, s, H-3), 6.62 (1H, s, H-2), 7.13–7.15 (2H, m, Ph), 7.18 (1H, m, Ph), 7.29–7.32 (2H, m, Ph); δ_C: 10.2+, 22.8+, 99.4+, 116.3, 125.1+, 125.4+, 128.0+, 147.3; ν_{max}: 3078 w, 3059 w,

3024 s, 2914 s, 2849 w, 1941 w, 1783 s, 1603 s, 1491 s, 1451 s, 1350 w, 1277 w, 1139 m, 1074 w, 1050 w, 1030 m, 1004 m, 962 w, 926 m, 769 s, 699 s cm^{-1}; *m/z*, %: 131 (M^++1, 0.07), 130 (M^+, 0.6), 129 (M^+−1, 1.5), 99 (48), 85 (31), 83 (46), 81 (100), 79 (69), 77 (15), 69 (21), 67 (44). Cyclopropene **31**[30b] (from the mixture with **2**) showed δ_H: 2.08 (6H, s, 2×CH_3), 2.42 (1H, s, H-3), 7.13–7.32 (5H, m, Ph); δ_C: 8.9+, 25.5+, 106.8, 147.3; ν_{max}: 1886 m cm^{-1}.

*4.13.2. Reaction of **18** with BnBr in the presence of HMPA.* HMPA (0.33 mL, 333 mg, 1.86 mmol, 2.2 mol equiv) was added dropwise to an ethereal solution of **18** at −60 °C. The mixture was stirred for 5 min at −60 °C followed by addition of benzyl bromide (157 mg, 0.92 mmol, 1.1 mol equiv) in dry ether (2 mL). The resulting solution was stirred for 15 h at rt, then cooled down to 0 °C and quenched with satd aq NH_4Cl (4 mL). The organic layer was separated, the aqueous layer was extracted with ether (5 mL). The combined organic layers were washed with brine (5 mL), dried and evaporated to give orange oil (174 mg), which contained (by ^1H NMR) cyclopropene **2**, benzyl bromide and dibenzyl **32** in molar ratio 1:1:0.5. Purification of 138 mg of the mixture on silica (pentane) afforded cyclopropene **2** (27 mg, 31%, R_f 0.43), benzyl bromide (50 mg, R_f 0.38) and dibenzyl **32** (24 mg, R_f 0.28) as colourless oils. Compound **32** showed *m/z*, %: 183 (M^++1, 2.8), 182 (M^+, 18), 91 (100), 77 (4), 65 (18), 51 (5). The spectral data of **2** were identical to that obtained above (Section 4.13.1).

*4.13.3. 2-(3-Phenylcyclopropenyl)-propane-2-ol (**3**) and 4-hydroxy-4-methylpentane-2-one (**33**).* Acetone (0.5 mL, 396 mg, 6.8 mmol, 8.0 mol equiv) was added dropwise to an ethereal solution of **18** at −60 °C. The mixture was stirred for 5 min at −60 °C, allowed to reach rt, stirred for 30 min, cooled to −10 °C and quenched with satd aq NH_4Cl (4 mL). The organic layer was separated, the aqueous layer was extracted with ether (2×3 mL). The combined organic layers were washed with brine (5 mL), dried and evaporated to give by ^1H NMR spectroscopy an equimolar mixture (176 mg) of cyclopropene **3** and compound **33**[42] as brown oil. Alcohol **3** (106 mg, 0.61 mmol, 73% by ^1H NMR spectroscopy) (Found M^+: 174.1061. $C_{12}H_{14}O$ requires: 174.1045) showed δ_H: 1.44 (3H, s, CH_3), 1.48 (3H, s, CH_3), 2.10 (1H, br s, OH), 2.81 (1H, d, *J*=1.6 Hz, H-3), 6.69 (1H, d, *J*=1.6 Hz, H-2), 7.12–7.28 (5H, m, Ph); δ_C: 24.3+, 28.5+, 28.7+, 69.7, 97.8+, 108.5, 125.4+, 125.4+, 128.0+, 146.2; *m/z* (GC/MS), %: 175 (M^++1, 0.27), 174 (M^+, 2), 173 (M^+−1, 0.3), 159 (6), 158 (17), 156 (40), 155 (9), 143 (51), 142 (12), 141 (100), 131 (22), 129 (13), 128 (35), 116 (16), 115 (54), 103 (4), 91 (11), 77 (5), 59 (8). The mixture showed ν_{max}: 3422 br s, 3059 w, 3025 w, 2975 s, 2929 m, 1769 m, 1701 s, 1601 m, 1493 m, 1452 m, 1364 s, 1211 m, 1178 s, 1071 w, 1021 w, 965 m, 913 m, 766 s, 700 s cm^{-1}. Compound **33** (from the mixture with **3**) showed δ_H: 1.28 (6H, s), 2.20 (3H, s), 2.65 (2H, s), 3.82 (1H, br s).

*4.13.4. 4-Phenylpentyne-2 (**34**).* $ZnCl_2$ (231 mg, 1.70 mmol, 1.5 mol equiv) in dry THF (1 mL) was added dropwise at −85 °C to a solution of **18** prepared from tribromide **13** (400 mg, 1.13 mmol) and MeLi in ether (1.77 mL, 2.48 mmol, 1.40 M, 2.2 mol equiv) in dry THF (10 mL) accordingly 4.13. Then the mixture was allowed to reach rt, stirred for further 30 min and transferred via cannula in the flask contained a mixture of iodobenzene (231 mg, 1.13 mmol, 1.0 mol equiv) and $Pd(PPh_3)_4$ (65 mg, 0.057 mmol, 5 mol %) in dry THF (2 mL). The resulting solution was stirred for 21 h at rt, diluted with pentane (10 mL) and filtered through a pad of silica (3 g). The solvent was removed to give yellow oil (271 mg), which contained (by ^1H NMR spectroscopy) cyclopropene **2**, iodobenzene and 4-phenylpentyne-2 **34**[43] in ratio 2.6:2.3:1 correspondingly. Part of the mixture (214 mg) was columned on silica (pentane) to afford iodobenzene (89 mg, R_f 0.57, t_R 4.66 min), **2** (18 mg, 16%, R_f 0.43) and **34** (13 mg, 10%, R_f 0.26, t_R 6.26 min) as colourless oils. Acetylene **34** showed δ_H: 1.48 (3H, d, *J*=7.2 Hz, CH_3), 1.88 (3H, d, *J*=2.2 Hz, CH_3), 3.74 (1H, qq, *J*=7.2, 2.2 Hz, H-4), 7.23–7.42 (5H, m, Ph); δ_C: 3.6+, 24.6+, 31.9+, 77.5, 82.1, 126.5+, 126.8+, 128.4+, 144.0; ν_{max}: 3084 w, 3061 w, 3026 m, 2974 s, 2918 s, 2870 m, 1946 w, 1873 w, 1804 w, 1600 w, 1494 s, 1450 s, 1370 w, 1340 w, 1300 w, 1264 w, 1151 w, 1077 w, 1042 w, 1026 m, 910 m, 759 s, 734 m, 699 s cm^{-1}; *m/z*, %: 145 (M^++1, 4.3), 144 (M^+, 37), 143 (M^+−1, 5.8), 130 (10), 129 (100), 128 (78), 127 (31), 115 (12), 102 (9), 77 (17), 63 (12), 51 (22). Iodobenzene showed *m/z*, %: 205 (M^++1, 9), 204 (M^+, 100), 127 (I^+, 18), 77 (78), 51 (40). The spectral data of **2** were identical to that obtained above (Section 4.13.1).

4.14. Computational studies

Details of the computational methods and the results obtained are provided as Supplementary data.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2009.09.098.

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