SHORT PAPER

J. Chem. Research (S), 2003, 21-23

Evidence for the formation of a new five-membered ring cyclic allene: Generation of 1-cyclopenta-1,2-dien-1-ylbenzene

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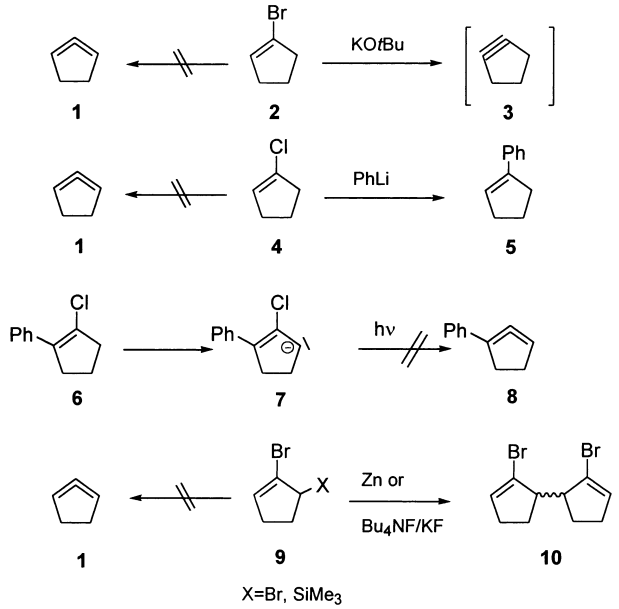
Treatment of 1-(2-iodocyclopent-1-en-1-yl)benzene (**13**), dissolved in benzene, with potassium *t*-butoxide resulted in the formation of 1-(2-phenylcyclopent-1-en-1-yl)benzene (**15**) and 1-cyclopent-1-en-1-ylbenzene (**5**) in a ratio of 1:1.

Keywords: cyclic allenes, elimination, radicals and radical reactions

One of the most efficient methods for the generation of cyclic strained allenes is the reaction of the corresponding vinylhalides with bases.[1] Favorskii first attempted to prepare 1,2-cyclopentadiene (**1**) by treatment of vinylbromide **2** with KO*t*Bu and obtained cyclopentyne **3** rather than allene **1** (Scheme 1).[2,3] Montgomery and Applegate have examined the reaction of 1-chlorocyclopentene (**4**) with phenyllithium.[4] They have shown that the coupling product **5** is formed by means of an elimination-addition mechanism proceeding *via* cycloalkyne intermediate. Tolbert *et al*.[5] and Johnson *et al*.[5] have reported that the photoexcitation of allyl anions results in an increased charge density at C-2. As a consequence, substitution at this position by an efficient leaving group should provide allenes.



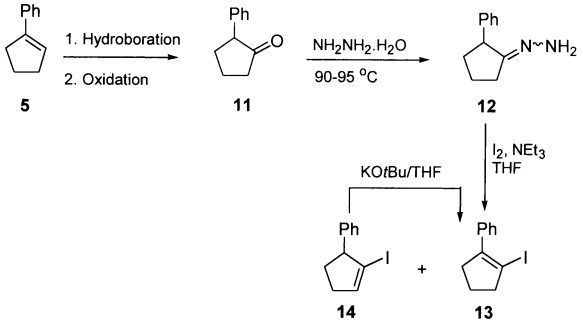
Scheme 1

They have succeeded in the generation of a six-membered ring allene. However, there was no evidence that the irradiation of **7** provided 1-cyclopenta-1,2-dien-1-ylbenzene (**8**). Ceylan *et al*.[6] attempted to prepare this highly strained allene **1** by treatment of **9** with zinc and fluoride ion, a technique that does succeed for larger ring allenes (Scheme 1).

More recently, we have applied Doering–Moore–Skatebol reaction to a bromofluorocyclopropane derivative and succeeded for the first time in the generation of five-membered ring allene derivative.[7]

After the failure of all elimination reactions to generate an allene from vinylhalides, we decided to force the system to undergo allene formation by replacing the double bond proton in **2** with a phenyl group. In this communication, we report evidence for the formation of a new five-membered ring cyclic allene, namely 1-phenyl-cyclopenta-1,2-diene (**8**), by treatment of 1-(2-iodocyclopent-1-en-1-yl)benzene (**13**) with KO*t*Bu at 240 °C.

In this synthesis, the vinyliodide **13** was selected as the key intermediate, having an efficient leaving group. For the synthesis of **13**, alkene **5** was used as the starting material. Bromobenzene was converted to the Grignard reagent, which was condensed with cyclopentanone. Dehydration of the crude alcohol with *p*-TsOH in benzene gave alkene **5** in 71% overall yield (Scheme 2).[8] Hydroboration of **5** followed by oxidation with PCC gave ketone **11**, which was converted to the isomeric hydrazone derivative **12** by treatment with hydrazine hydrate at 90–95 °C. Product **12** was estimated to be a 2:1 mixture of *E* and *Z* isomers. Treatment of the isomeric mixture of **12** with iodine[9] in the presence of NEt_3 in THF resulted in the formation of two products **13** and **14** in a ratio of 8:3 (40% total yield), which were separated by silica gel column chromatography. The mixture consisting of **13** and **14** was treated with KO*t*Bu at the reflux temperature of THF. The vinyl iodide **14** was completely isomerised to **13**. The aromatic proton signals in the NMR spectrum of **13** appear at δ 7.2–7.6 as a multiplet. The methylenic protons resonated at δ 2.81 (br. triplet), 2.67 (br. triplet), and 1.98 (quintet, J = 7.6 Hz), in accordance with the proposed structure. Six resonance signals in the sp^2 region of the ^{13}C NMR spectrum of **13** confirmed the presence of a fully substituted double bond.



Scheme 2

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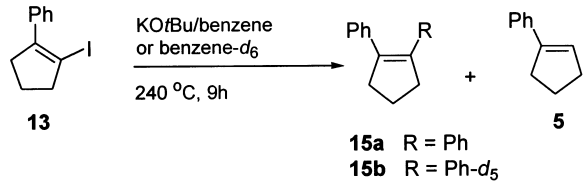
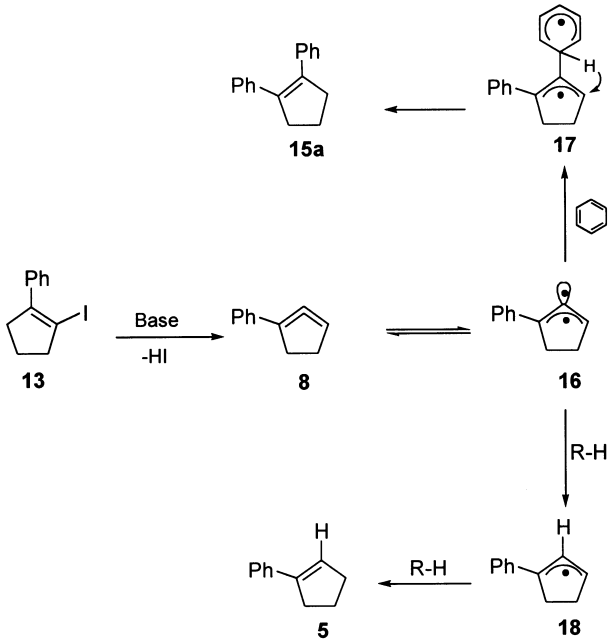
† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

After the successful synthesis of the key compound **13,** it was submitted to the base-induced HI-elimination reaction. No reaction was observed when the dehydroiodonation was carried out in different solvents and at different temperatures (60–200°C). When more drastic conditions (sealed tube, benzene, 240°C) were employed, dehydroiodonation occurred and 1-(2-phenylcyclopent-1-en-1-yl)benzene (**15a**) and **5** were formed in a ratio of 1:1 (total yield 45%). The latter is the result of a reductive elimination reaction (Scheme 3).



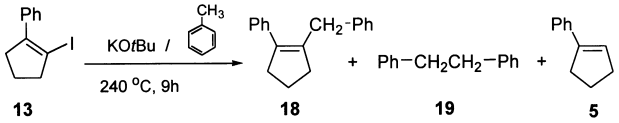
Scheme 3

The structure of **15a** was established by comparison of the NMR data with those reported in the literature.[10] An interesting feature of this reaction was the incorporation of a second phenyl group in the molecule. In order to determine the source of the second phenyl group (arising from the solvent or from the starting material **13**), the reaction was run under the same conditions in fully deuterated benzene. The same products were formed in the same ratio. The integration of the aromatic protons of **15b** (the integration value was reduced to half of **15a**) clearly indicated that the phenyl group was incorporated from the solvent molecule. On the basis of these results, the following mechanism for the formation of **15a** and **5** was suggested.



Scheme 4

Firstly, base-induced elimination of HI from **13** gives the intermediate, allene **8**, which will be in equilibrium with the corresponding diradical **16** (Scheme 4). Theoretical calculations show that 1,2-cyclopentadiene **1** may exist as a chiral allenic structure, but it can easily racemise through a species best described as a diradical (inversion barrier of 2-5 kcal/mol).[11] The effect of temperature on the racemisation of the allenic structure was also demonstrated in the case of six- and seven-membered ring allenes.[12] Recently, Tolbert *et al.* and Houk *et al.* have presented convincing theoretical evidence that the diradical stepwise pathways are preferred over the concerted path in the trapping reaction of 1,2-cyclohexadiene with 1,3-butadiene and furan.[13] More recently, diradical structures have been postulated in the cyclisation reactions in the electrocyclic ring closure of some dieneyenes.[14] The diradical **16** can add to benzene to give the intermediate **17** which can be easily transformed to the neutral compound, diphenylalkene **15a**, by a proton transfer (Scheme 4).



Scheme 5

To support the formation of diradical intermediate, the base-induced HI elimination reaction was carried out in toluene as described above (Scheme 5). Analysis of the product mixture indicated the formation of **18** (17%), **19** (7%) and **5** (5%). The formation of dibenzyl (**19**) can be explained only with the formation of the benzyl radical, which can easily form the dimer **19**. The formation of product **18** can be rationalised as described above in Scheme 4.

In conclusion, we assume that the HI elimination gave the strained five-membered ring allene **8**, which is in equilibrium with the diradical intermediate **16**. This intermediate is intercepted by benzene ring (benzyl radical) followed by proton abstraction to provide the diphenyl alkenes **15a** and **18**, respectively. Further work to support the electronic nature of this intermediate is in progress.

Experimental

2-Phenylcyclopentanol: To a slurry of $NaBH_4$ (1.8g, 47.37 mmol) in THF (60 ml) was added alkene **4** (6g, 41.66 mmol) in THF (30 ml) at room temperature under N_2. The reaction mixture was cooled to 0°C and added BF_3–OEt_2 (6.7g, 47.22 mmol) during 30 min. and the resulting mixture was stirred at room temperature for 3h. Then, to the mixture was added NaOH (21 ml, 3N) and H_2O_2 (24 ml, 30%), and warmed to 50°C, stirred for 30 min. The aqueous layer was extracted with diethyl ether (2x150 ml). The combined organic extracts were washed with of Na_2SO_3 solution (2%) and dried ($MgSO_4$). Removing of the solvent gave 2-phenylcyclopentanol (colourless liquid, 5.5g, 81%). ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.28 (m, 5H), 4.12 (m, 1H), 2.87 (m, 1H), 2.36 (m, 1H), 2.11 (m, 2H), 1.79 (m, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ = 144.0, 129.0 (2C), 128.0 (2C), 126.8, 80.8, 54.8, 34.5, 32.4, 22.3. IR (NaCl, film, cm^{-1}) 3600, 3020, 2950, 2860, 1480, 1450, 1080, 1030, 690. Anal. Calcd for $C_{11}H_{14}O$: C, 81.44 ; H, 8.70. Found : C, 81.23 ; H, 8.91.

2-Phenylcyclopentanone 11: To a stirred solution of pyridinium-chlorochromate (PCC) (12g, 55.68 mmol) in 50 ml CH_2Cl_2 was added the alcohol (prepared above) (8g, 49.38 mmol) in 25 ml CH_2Cl_2 at 0°C for 30 min. The mixture was stirred for 3h. at room temperature, then filtered. Organic layer was washed with water (100 ml) and dried (Na_2SO_4). Removing of the solvent gave 2-phenylcyclopentanone **11** (6.3g, 80%). ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.27 (m, 5H), 3.33 (t, *J* = 8.7 Hz, 1H), 2.50 (m, 2H), 2.02 (m, 4H). ^{13}C-NMR (50 MHz, $CDCl_3$) δ = 218.5, 139.0, 129.1 (2C), 128.6 (2C), 127.4, 55.8, 39.0, 32.2, 21.4. IR (NaCl, film, cm^{-1}) 3090, 3030, 2960, 2870, 1740, 1450, 1405, 1140, 1040, 700. Anal. Calcd for $C_{11}H_{12}O$: C, 82.46 ; H, 7.55. Found : C, 82.36 ; H, 7.49.

syn- and anti 2-phenylcyclopentan-1-one hydrazone: A solution of hydrazine hydrate (1.97 g, 39.4 mmol) was a added to a vigorously stirred solution of 2-phenylcyclopentan-1-one (6.3 g, 39.4 mmol) at room temperature over three minutes. The reaction mixture was stirred at 90–95°C for 1 hr. The reaction mixture was cooled to room temperature and extracted with chloroform (3x). The combined extract was dried with K_2CO_3 and the solvent was evaporated to yield essentially pure mixture consisting of *syn-* and *anti*-hydrazone **12** (colourless liquid, 6.7 g, 97.8%). ^{1}H NMR (400 MHz, $CDCl_3$) δ =

7.25 (m, 10H), 4.87 (br. s, NH_2, 2H), 4.68 (br. s, NH_2, 2H), 3.68 (t, 1H), 3.64 (t, 1H), 2.65–1.59 (m, 12H). ^{13}C NMR (50 MHz, $CDCl_3$) δ = 162.5, 160.9, 143.2, 141.8, 129.7, 128.9 (2C), 128.8, 128.7, 127.9, 127.4, 126.9, 51.2, 45.9, 38.0, 35.6, 35.27, 27.01, 23.4.

1-(2-iodocyclopent-1-en-1-yl)benzene: A saturated solution of iodine (19.56 g, 77 mmol) in dry THF was added rapidly to a stirring solution of isomeric **12** (6,7 g, 38.50 mmol) in 75 ml triethylamine under nitrogen atmosphere at 0°C. The reaction mixture was stirred for an additional hour at room temperature. After diluting the reaction mixture with 300 ml distilled water, it was extracted with hexane (3×100 ml). The combined organic layers were washed with HCl (3×100 ml, 1N), saturated $NaHCO_3$ and NaCl solution, dried and evaporated to yield a mixture (5.7 g) consisting of **13** and **14**. The residue was submitted to silica gel column chromatography using silica gel (60 g) and eluting with hexane. Early fractions yielded pure 1-(2-iodocyclopent-1-en-1-yl)benzene (**13**) (colourless liquid, 2.0 g, 19.25%). %). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.44 (m, aromatic, 2H), 7.22 (m, aromatic, 3H), 2.81 (m, methylenic, 2H), 2.67 (m, methylenic, 2H), 1.98 (quintet, *J* = 7.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 146.4, 138.1, 129.4 (2C), 128.2 (2C), 128.6, 91.8, 47.5, 37.1, 24.5. IR (NaCl, film, cm^{-1}) 3080–3010, 2960–2840, 1470, 1440. Anal. Calcd for $C_{11}H_{11}I$: C, 48.91 ; H, 4.10. Found: C, 48.74; H, 4.03.

Later fractions were mixtures. The last fraction yielded pure 1-(2-iodocyclopent-2-en-1-yl)benzene (**14**) (2.3g 22%). ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.28 (m, aromatic, 5H), 6.35 (m, olefinic, 1H), 3.93 (m, 1H), 2.49 (m, 3H), 2.01 (m, 1H). ^{13}C NMR (50 MHz, $CDCl_3$) δ = 144.6, 141.8, 129.1 (2C), 128.3, (2C), 127.3, 100.8, 60.1, 34.6, 33.6. IR (NaCl, film, cm^{-1}) 3080, 3020, 2960, 2850, 1600, 1530, 1480, 1450. Anal. Calcd for $C_{11}H_{11}I$: C, 48.91 ; H, 4.10. Found: C, 49.34; H, 4.27.

Base-supported isomerisation of **14***:* A mixture (4 g) consisting of **13** and **14** (1:1) was dissolved in 50 ml of dry THF and 2 g of *t*-BuOK was added. The resulting mixture was refluxed for 15 h. After evaporation of the solvent the residue was submitted to silica gel column chromatography using silica gel (30 g) and eluting with hexane. Evaporation of the solvent gave **13** in quantitative yield.

Reaction of **13** *with t-BuOK in benzene; Synthesis of 1-(2-phenylcyclopent-1-en-1-yl)benzene* **(15)***:* A solution of **13** (200 mg, 0.74 mmol) in 3 ml of dry benzene and 90 mg of *t*-BuOK was placed in a glass tube. After sealing the tube, it was heated to 240°C for 9 hours. Benzene was evaporated and the residue was submitted to silica gel (20 g) column chromatography eluting with hexane. The first fraction yielded pure 1-cyclopent-1-en-1-ylbenzene (**5**) (33 mg, 22.3%) and the second fraction gave 1-(2-phenylcyclopent-1-en-1-yl)benzene (colourless crystals from methanol, m.p. 56–57°C (m.p. 59°C[9]), 2.0 g, 19.25%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.19 (m, aromatic, 10H), 2.84 (t, methylenic, *J* = 7.5 Hz, 4H), 1.98 (qt, *J* = 7.5 Hz, methylenic, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ = 138.9 (2C), 138.0 (2C), 128.6 (4C), 128.5, (4C), 127.0 (2C), 39.6 (2C), 22.6. MS *m/z:* 220 (M^+, 100), 219 (85), 205 (32), 191 (30), 141 (40), 129 (47), 115 (42), 91 (56).

Reaction of **13** *with t-BuOK in deuterated benzene; synthesis of* **15b:** The same reaction was carried out in deuterated benzene as reported above. The product analysis was carried out by GC/MS and NMR.

Reaction of **13** *with t-BuOK in toluene:* A solution of **13** (230 mg, 0.85 mmol) in 3 ml of dry toluene and 120 mg (1.07 mmol) *t*-BuOK was placed in a glass tube. After sealing the tube, it was heated to 240°C for 9 hours. Toluene was evaporated and the residue was submitted to silica gel (25 g) column chromatography eluting with hexane. The first fraction yielded cyclopent-1-enyl-benzene (**5**) (25 mg, 20.4%) and the second fraction gave a mixture of **18** and **19** (38 mg) which was analysed by GC/MS. The NMR data of **18** has been extracted from the NMR spectrum of the mixture. **18:** ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.20 (m, aromatic, 5H), 3.1 (s, methylenic, 2H), 2.1–1.9 (m, methylenic 4H), 1.5 (qt, methylenic 2H). MS *m/z:* 234 (M^+, 100), 219 (45), 192 (15), 191 (29), 143 (16), 128 (24), 115 (28), 102 (18), 91 (39).

The authors are indebted to Middle East Technical University (Grant AFP-2000-08) and Scientific Technical Research Council of Turkey (Grant TUBITAK-MISAG-216) for financial support of this work

Received 9 March 2002; accepted 12 July 2002
Paper 02/1285

References

1 (a) M. Balci and Y. Taskesenligil, In *Advances in Strained and Interesting Organic Molecules;* B. Halton, Ed.; JAI Press Inc. 2000, Vol. 8, pp 43-81; (b) R.P. Johnson, *Chem. Rev.* 1989, **89**, 1111.
2 A.E. Favorskii, J. Gen. Chem. USSR (Engl. Transl.), 1936, 6, 720.
3 G. Wittig and J. Heyn, *Justus Liebigs Ann. Chem.*, 1972**, 756**, 1.
4 (a) L.K. Montgomery, F. Scardiglia and J.D. Roberts, *J. Am. Chem. Soc.*, 1965**, 87**, 1917; (b) L.K. Montgomery and L.E. Applegate, *J. Am. Chem. Soc.*, 1967**, 89**, 2952.
5 L.M. Tolbert, M.N. Islam, R.P. Johnson, P.M. Loiselle and W.C. Shakespeare, J. Am. Chem. Soc., 1990, **112**, 6416.
6 M. Ceylan, H. Seçen and Y. Sütbeyaz, *J. Chem. Research (S)*, 1993, 70.
7 F. Algi, R. Özen and M. Balci, *Tetrahedron Lett.* 2002, **43**, 3129.
8 C.H. DePuy, G.F. Morris, J.S. Smith and R.J. Smat, *J. Am. Chem. Soc.*, 1965, **87**, 2421.
9 For conversion of ketones into vinyl iodides see: (a) D.H.R. Barton, R.E. O'Brien and S. Sternhell, *J. Chem. Soc.* 1962, 470; (b) A. Pross and S. Sternhell, *Aust. J. Chem.*, 1970, **23**, 989.
10 (a) F. Jachimowicz, G. Levin and M. Szwarc, *J. Am. Chem. Soc.*, 1977, **99**, 5977; (b) G.H. Jeffery and A.I. Vogel, *J. Chem. Soc.*, 1948, 1804.
11 R.O.Jr. Angus, M.W. Schmidt and R.P. Johnson, *J. Am. Chem. Soc.* 1985**, 107**, 532.
12 M. Balci and W.M. Jones, *J. Am. Chem. Soc.*, 1980, **102**, 7607.
13 M. Nendel, L.M. Tolbert, L.A. Herrig, Md N. Islam and K.N. Houk, *J. Org. Chem.*, 1999, **64**, 976.
14 (a) M. Fernandez-Zertuche, R. Hernandez-Lamoneda and A. Solis-Ramirez, *J. Org. Chem.*, 2000, **65**, 5207.; (b) H.W. Moore and Y. Xiong, *J. Org. Chem.*, 1996, **61**, 9168.; (c) H.W. Moore, H. Xia and Y. Xiong, *J. Org. Chem.* 1995, **60**, 6460.