# Preparation of arylspiro[2.4]hept-5-enes from aryldibromocyclopropanes via diallylation and metathesis reaction

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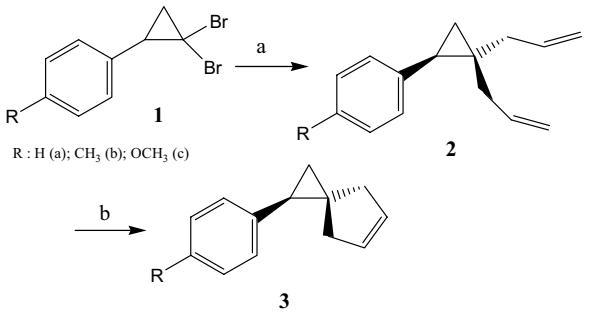
A series of arylspiro[2.4]hept-5-enes can be prepared from aryl-diallylcyclopropanes by using Grubbs' catalyst in good yields.

**Keywords:** arylspiro[2.4]hept-5-ene, Grubbs' catalyst, dihalocyclopropane

Dihalocyclopropanes are versatile intermediates. Alkylation of halocyclopropanes provides us with an effective route to a variety of functionalised cyclopropane derivatives.[1] The transformation of *gem*-dihalocyclopropanes into 1-alkyl-1-butylcyclopropanes has been reported to proceed by successive treatment with dibutylcupurate or tributylzincate and several electrophile.[2] We now report the double allylation of *gem*-dibromocyclopropanes for preparing the spiro[2.4]heptenes, which can be further functionalised by reaction of the double bond of the five-membered ring.

In this study, we found that the allenes were the products from coupling of either vinyl magnesium bromide or allyl magnesium bromide as well as the Grignard reagent prepared from dibromocyclopropanes.[3] Same results were also observed from the reaction of lithium allylate and 1,1-dibromo-2-arylcyclopropane prior to adding of $Cu_2I_2$. Those results are consisted with the reports on the reactions of halogen of halocyclopropanes with strong base to form an anion which can be trapped by an electrophile at –100°C.[2c] This is a drawback in the functionalised of *gem*-dihalocyclopropanes *via* direct addition of either Grignard reagent or alkyl lithium.




(a) $C_6H_5OCH_2CH{=}CH_2$/Li, 258 K, 2h; Cu(I)I, 235 K, 1h;
(b) Grubbs' catalyst, 363 K, 12h.

Allyl phenyl ether was used instead of allylic bromide to prepare lithium allylate. Lithium diallylcuprate was obtained from the reaction of lithium allylate and Cu(I)I at –30°C. To which dibromocyclopropane (**1**) was added at –78°C and allowed to react for 12 h to form diallylcyclopropanes (**2**) in good yields without ring-opening product. In this system, *gem*-dibromocyclopropane were reacted first with lithium diallylcuprate and then with lithium allylate.

The applications of olefin metathesis for organic syntheses have been applied extensively.[4] Grubb's catalyst ($RuCl_2$ (=CHPh)$(PCy_3)_2$, Cy = cyclohexyl), an active, long-life, environmentally friendly, low sensitive and high tore to most functional groups, has been applied for the preparation of cycloalkenes via the ring-closing metathesis process.[5,6] A series of arylspiro[2.4]heptenes (**3**) were prepared from the corresponding 1,1-diallyl-2-arylcyclopropanes by using Grubb's catalyst in near quantitative yields. The carbon–carbon double bond of spiroheptene is a potential functionality for organic transformation.

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## Experimental

All melting points were measured with a Yanaco MP-J3 apparatus and are uncorrected. $^1$H NMR and $^{13}$C NMR spectra were recorded on a Bruker Advance 400 spectrometer at 400 and 100 MHz, respectively, at ambient temperature unless specified. Chemical shifts for samples in $CDCl_3$ solution are reported in δ units relative to using the residual proton and carbon resonance of the solvent. Mass spectra were obtained from GC/MS (Fisons 8000 series coupled with Finnigan MD-800) at an ionisation potential of 70 eV. Microanalyses were carried on a Heraeus CHN–O rapid analyser at the Instrumental Analytic Centre at the National Chung Hsien University. The Grubbs' catalyst was prepared from the reaction of tris(triphenylphosphine)ruthenium chloride and phenyldiazomethane followed by exchanging by tricyclohexylphosphine according to the literature.[7] 1-Aryl-2,2-dibromocyclopropanes were prepared from the reactions of corresponding styrenes and bromoform.[8]

*Typical procedure for preparation of 1,1-diallyl-2-arylcyclopropanes* (**2**)

This reaction was carried out in the pre-dried system under a stream of nitrogen gas. A lithium allylate solution was prepared from lithium (0.56 g, 90 mmol) and allyl phenyl ether (3.02 g, 30 mmol) in THF (20 ml) at –15°C for 2 h. In this stage, the dark red solution was obtained. After it was cooled to –38°C, solid $Cu_2I_2$ (2.85 g, 15 mmol) was added *via* a side-arm introducer followed by stirring for 30 min. This grey–green mixture was allowed to cool down to –78°C, 1,1-dibromo-2-phenylcyclopropane(1.37 g, 5 mmol) in THF (5 ml) was added. After stirring at that temperature for 12 h, the mixture was quenched with ice-water (30 ml) and then extracted with diethyl ether (3 x 30 ml). The combined organic layer was dried over $MgSO_4$, filtered, concentrated to give the crude product with orange colour. The product was primary purified by washing through silica gel column with *n*-hexane to give 0.92 g colourless waxy material, which contains 1,1-diallyl-2-phenylcyclopropane **2a (**85%) and 1-bromo-2-phenylcyclopropanes (15%) based on the areas ration by GC–MS analysis. The further purification by HPLC (RP-18, 250 mm × 20 mm, 10 μm) with MeOH: $H_2O$ = 10: 1 as an eluent to give pure compound **2a** (0.65 g, 65% yield); m.p. 28–29°C; $^1$H NMR (600 MHz) δ 0.85 (1H, dd, *J* = 5.4, 8.4 Hz); 0.93 (1H, t, *J* = 5.4 Hz), 1.54(1H, dd, *J* = 6.6, 14.4 Hz), 1.91(1H, dd, *J* = 6.6, 14.4 Hz), 1.97(1H, dd, *J* = 6.6, 14.4 Hz), 2.03 (1H, dd, *J* = 6.6, 8.4 Hz), 2.33(1H, dd, *J* = 6.6, 14.4 Hz), 4.89(1H, dd, *J* = 2.4, 10.2 Hz), 4.95(1H, dd, *J* = 2.4, 17.4 Hz), 5.08(1H, d, *J* = 3.6 Hz), 5.10(1H, s), 5.64(1H, ddt, 6.6, 10.2, 16.8 Hz), 5.89(1H, ddt, *J* = 6.6, 11.4, 16.8 Hz), 7.17(3H, m), 7.27(2H, t, *J* = 7.2 Hz); $^{13}$C NMR δ 15.7, 26.3, 28.2, 35.4, 41.5, 116.0, 116.6, 125.7, 127.9, 129.0, 136.1, 136.5, 139.3; MS (*m/z*,%) 198($M^{+\cdot}$, 4), 157(50), 129(57), 115(100), 104(44), 91(91), 77(43); Anal. Calcd. for $C_{15}H_{18}$: C, 90.85; H, 9.15. Found: C, 90.79; H, 9.20.

*1,1-Diallyl-2-(4-methylphenyl)cyclopropane* **2b**: Yield 74%; m.p. 32–34°C; $^1$H NMR δ 0.82 (1H, dd, *J* = 5, 8 Hz); 0.88(1H, t, *J* = 5 Hz), 1.54(1H, 1H, dd, *J* = 7, 11 Hz), 2.00(1H, dd, *J* = 6, 8 Hz), 2.30(3H, s), 2.35(1H, dd, *J* = 8, 14 Hz), 4.91(1H, dd, *J* = 2.4, 17 Hz), 5.08(1H, d, *J* = 4 Hz), 5.65(1H, m), 5.90(1H, m), 6.84(2H, d, *J* = 7 Hz), 6.97(2H, d, *J* = 7 Hz); $^{13}$C NMR δ 15.3, 15.6, 26.8, 27.7, 30.3, 35.5, 115.6, 115.9, 125.6, 128.8, 129.0, 134.5, 136.2, 136.4; MS(*m/z*,%) 212($M^{+\cdot}$, 3), 171(52), 129(100), 118(31), 105(75), 91(34); Anal. Calcd. for $C_{16}H_{20}$: C, 90.51; H, 9.49. Found: C, 90.22; H, 9.58.

*1,1-Diallyl-2-(4-methoxyphenyl)cyclopropane* **2c**: Yield 80%; m.p. 35°C; $^1$H NMR δ 0.83(2H, m); 1.53 (1H, dd, *J* = 7, 15 Hz), 1.95(3H, m), 2.33(1H, dd, *J* = 7, 14 Hz), 3.79(3H, s), 4.92(2H, m), 5.06(1H, d, *J* = 4 Hz), 5.09(1H, m), 5.66(1H, ddt, *J* = 7, 10, 15 Hz), 5.89(1H, ddt, *J* = 7, 10, 14 Hz), 6.82(2H, d, *J* = 8 Hz), 7.09(2H, d, *J* = 8 Hz); $^{13}$C NMR δ 15.7, 25.9, 27.4, 35.5; 41.4, 55.2, 113.4, 115.9, 116.5, 130.3, 136.2, 136.6, 157.7; MS(*m/z*, 5) 228($M^{+\cdot}$, 8), 187(76), 145(100), 134(41), 121(86), 77(32); Anal. Calcd. for $C_{16}H_{20}O$: C, 84.16; H, 8.83. Found: C, 83.93; H, 9.01.

*Typical procedure for the preparation of 1-aryl-spiro[2.2]hept-5-ene* (**3**)

1-Phenylspiro[2.4]hept-5-ene **3a**. A mixture of 1,1-diallyl-2-phenylcyclopropane **2a** (0.198 g, 1 mmol) and Grubbs' catalyst (0.041 g, 0.005 mmol) in toluene (2 ml) was stirred at 90°C under a nitrogen atmosphere for 12 h. During the reaction, the solution was maintained in deep violet colour. After the reaction, the catalyst was removed by filteration through a silica gel column with *n*-hexane as an eluent to give pure compound **3a** in 96% yield (0.16 g), m.p. 25–26°C; $^1$H NMR δ 1.09 (1H, t, *J* = 5 Hz), 1.17 (1H, dd, *J* = 5, 9 Hz), 2.12(3H, m), 2.47(1H, dt, *J* = 2, 16 Hz), 2.60(1H, dt, *J* = 2, 16), 5.70(1J, dt, *J* = 2, 4 Hz), 5.76(1H, dt, 2, 4 Hz), 7.10(2H, d. *J* = 7 Hz), 7.17(1H, t, *J* = 8 Hz), 7.28(2H, t, *J* = 8 Hz); $^{13}$C NMR δ 20.7, 28.2, 30.4, 37.5, 44.7, 125.4, 127.9, 128.0, 129.6, 130.5, 140.3; MS (*m/z*,%) 170($M^{+\cdot}$, 17), 128(23), 118(100), 91(34); Anal. for $C_{13}H_{14}$: C, 91.71; H, 8.29. Found: C, 91.78; H, 8.30.

*1-(4-Methylphenyl)spiro[2.4]hepta-5-ene* **3b**: 95% yield; m.p. 27–28°C; $^1$H NMR δ 1.04(1H, t, *J* = 5 Hz), 1.13(1H, dd, *J* = 5, 9 Hz), 2.10(3H, m); 2.32(3H, s), 2.45(1H, t, *J* = 3 Hz), 2.57(1H, t *J* = 3 Hz), 5.69(1H, dt, *J* = 3, 4 Hz), 5.75(1H, dt, *J* = 3, 4 Hz), 6.98(2H, d, *J* = 8 Hz), 7.08(2H, d, *J* = 8 Hz); $^{13}$C NMR δ 20.52, 21.4, 27.9, 30.0, 37.5, 44.7, 127.8, 128.6, 129.6, 130.5, 134.7, 137.4; MS(*m/z*, %) 184($M^{+\cdot}$, 17), 104(100), 91(12), 77(14); Anal. Calcd. for $C_{14}H_{16}$: C, 91.25; H, 8.75. Found: C, 91.21; H, 8.59.

*1-(4-Methoxyphenyl)spiro[2.4]-hepta-5-ene* **3c**: 92% yield; m.p. 28°C; $^1$H NMR δ 0.99(1H, t, *J* = 5 Hz), 1.11(1H, dd, *J* = 5, 8 Hz), 2.05(3H, m), 2.46(1H, t, *J* = 3 Hz), 2.53(1H, t, *J* = 3 Hz), 3.79(3H, s), 5.69(1H, dt, *J* = 3, 4 Hz), 5.74(1H, dt, *J* = 3, 4 Hz), 6.28(2H, d, *J* = 7 Hz), 7.01(2H, d, *J* = 7 Hz); $^{13}$C NMR δ 20.3, 27.6, 29.6, 37.5, 44.6, 55.3, 115.5, 128.9, 129.7, 130.5, 132.3, 157.6; MS(*m/z*,%) 200($M^{+\cdot}$, 24), 169(43), 134(100), 121(36); Anal. Calcd. for $S_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 83.88; H, 8.16.

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## References

1 (a) H.U. Reissig, In *The Chemistry of the Cyclopropyl Group*; S. Patai; Z. Rappoport, (eds); Wiley: London, 1987, p 375; (b) *Small Ring Compounds in Organic Synthesis I-IV*; A. de Meijere, ed.; Springer: Berlin, 1990; (c) H.N. Wong, M.Y. Hon, C.W. Tse, Y.C. Yip, J. Tanko and T. Hudlicky, *Chem. Rev*., 1989, **89**, 165; (d) H. Reißu. *Top. Curr. Chem*., 1988, **144**, 73; (e) A.J. Dulayymi, M.S. Baird, I.G. Bolesov, V. Tveresovsky and M. Rubin, *Tetrahedron Lett*., 1996, **37**, 8933; (f) A. Ogawa, S. Ohya and T. Hirano, *Chem. Lett*., 1997, 275.

2 (a) M.S. Baird, A.V. Nizovtsev and I.G. Bolesov, *Tetrahedron*, 2002, **58,** 1581; (b) H. Kakiya, R. Inoue, H. Shinokube and K. Oshima, *Tetrahedron*, 2000, **56**, 2131; (c) T. Hiyama, H. Yamamoto, K. Nishio, K. Kitatani and H. Nozaki, *Bull. Chem. Soc. Jp*., 1979, **52**, 3632; (d) K. Kitatani, T. Hiyama and H. Nozaki, *Bull. Chem. Soc. Jp*., 1977, **50**, 1600; (e) Y. Hishii, K. Wakasugi and Y. Tanabe, *Syn Lett*., 1998, 67.

3 R. Inoue, H. Shinokube and K. Oshima, *Tetrahedron Lett*., 1996, **37**, 5377.

4 T.M. Trnka and R.H. Grubbs, *Acc. Chem. Res*., 2001, **34**, 18.

5 (a). G.C. Fu, R.H. Grubbs and J.W. Ziller, *J. Am. Chem. Soc*., 1993, **115**, 3800; (b) S.T. Nguyen and R.H. Grubbs, *J. Am. Chem. Soc*., 1993, **115**, 9858; (c) R.H. Grubbs and S. Chang, *Tetrahedron*, 1998, **54**, 4413.

6 R.J. de Lang and L. Brandsma, *Synth. Comm*., 1998, **28**, 225.

7 P. Schwab, R.H. Grubbs and J.W. Ziller, *J. Am. Chem. Soc*., 1996, **118**, 100.

8 S.T. Lin and M.L. Lin, *J. Chem. Soc. Perkin Trans., 2*, 1990, 91.