

A convenient route to prepare isodicyclopentadiene—precursor of 1,5-dihydro-pentalene

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Abstract—A new route to prepare tricyclo[5.2.1.0^{2,6}]deca-2,4-diene (isodicyclopentadiene) was developed. This new route passes through a brominated (5-bromotricyclo[5.2.1.0^{2,6}]dec-3-ene) derivative obtained from tricyclo[5.2.1.0^{2,6}]dec-3-ene (8,9-dihydrodicyclopentadiene) and NBS with a good yield. The complete assignment of protons and carbons on nuclear magnetic resonance spectra was done for dicyclopentadiene and the chemically transformed compounds by 2D NMR techniques.
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1. Introduction

Recent reviews have shown that the poly-metallic species with a strong electronic interaction can be used in the preparation of materials utilized in electronic devices, magnetic devices or non-linear optic devices.¹ The bridge between metals is essential in order to reach intermetallic electronic interactions, and there are several possibilities of ligands to bond metals using π and σ bonds.² Our research interest is to focus on intermetallic interactions using rings of π fused type: pentalene, indacene and naphthalene. From these ligands, pentalene complexes exhibit one of the strongest interactions between metals coordinated to it, but the greatest difficulty is in use and preparation of this ligand.³ Katz was a pioneer in the chemistry of organometallic complexes of pentalene. Using 1,5-dihydro-pentalene, Katz was able to prepare a series of complexes, passing through an intermediate lithiated, and obtained iron,

cobalt and nickel derivatives, even a rhodium pentalene complex.⁴ One of the last preparations of pentalene available in the literature was developed by O'Hare,⁵ but in this Letter only the pentalene dianions are accessible.

The route to pentalene given by Katz begins with easily accessible materials, but with hard synthetic preparation routes. Our research group has taken parts of the original preparation of Katz and we have modified the preparation of isodicyclopentadiene, the immediate organic compound before 1,5-dihydropentalene.

Herein we describe an alternate route to obtain isodicyclopentadiene, and we characterize a brominated derivative to achieve isodicyclopentadiene.⁴

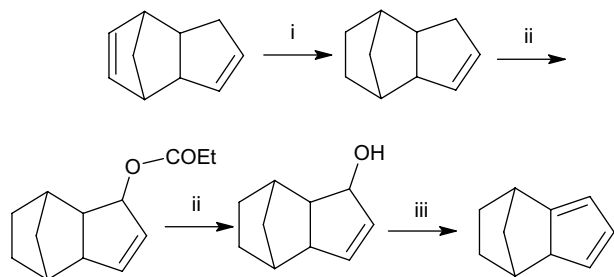
2. Results and discussion

Basically, the preparation of isodicyclopentadiene followed by Katz can be divided into three parts:

(i) Hydrogenation of the bond which causes more strain on the dicyclopentadiene, (ii) introduction of an easily leaving group at the allylic position and (iii) elimination of this cited group yielding a conjugate double bond and obtaining the desired compound (Scheme 1).

Keywords: Isodicyclopentadiene; 5-Bromo-8,9-dihydrodicyclopentadiene; Tricyclo[5.2.1.0^{2,6}]decadiene derivatives; NMR assignment.

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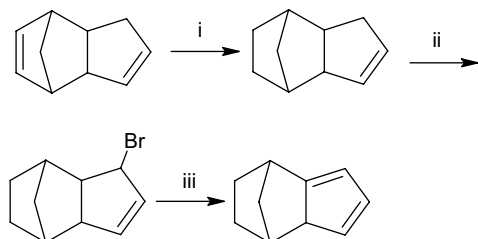


Scheme 1. Steps followed by Katz, Ref. 3. (i) Stage of hydrogenation, (ii) insertion of an outgoing group and (iii) elimination of an outgoing group.

Different conditions for hydrogenation, leaving group and eliminations, were studied. Between many hydrogenating catalysts we chose nickel based on its low costs and accessible raw materials. We found that the optimal working conditions are these: starting from 1.5 g of nickel acetate and an equimolar quantity of 1.0 M NaBH_4 to hydrogenate 30 g of dicyclopentadiene by batch. The resulting metallic nickel is suitable to hydrogenate double bonds and has the required selectivity. Larger or smaller quantities of nickel give a very fast or very slow hydrogenative reaction, respectively.

When the allylic is the desired position to transform chemically, one of the most popular and inexpensive agents used is *N*-bromosuccinimide, NBS. Bromination at this position and later HBr elimination, when there is hydrogen available, is a very clear way to form a double bond and in this case the conjugate double bonds belong to isodicyclopentadiene.⁷ Basically, this is the strategy used to modify the route followed by Katz.

The hydrogenated product was purified by recrystallization and mixed with equimolar amounts of NBS in CCl_4 , this reaction was made without initiators, peroxides, only the temperature of reflux was enough to initiate the reaction. This reaction affords a liquid that was purified in a column with silica, and chloroform as eluent. Elimination with some bases was tested and the only one that gave good yield was quinoline. When brominated product was heated with quinoline and later distilled at low pressure, a clear liquid was yielded and the NMR of this liquid was in agreement with the reported isodicyclopentadiene.⁴ The isomers were not separated because all of them were used to yield 1,5-dihydropentalene in a retro-Diels–Alder pyrolysis reaction carried out at 530 °C and at 0.1 mmHg of pressure (Scheme 2).



Scheme 2. Steps followed in this preparation. (i) Hydrogenation, (ii) insertion of outgoing group and (iii) elimination of outgoing group.

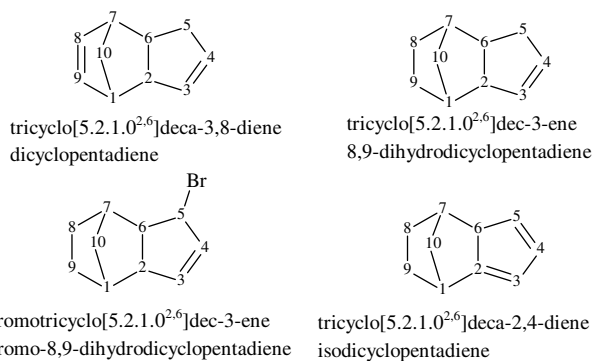


Figure 1. Numbering and name of the different compounds related with the syntheses.

The compounds were characterized principally by nuclear magnetic resonance spectroscopy. ^1H and ^{13}C assignments by NMR are not simple. These assignments were performed with 2-D NMR techniques, applying HH-COSY, HSQC, HMBC, because the spectra of superior order are present in this series of compounds. The 2D-NMR spectra were essential to elucidate assignments of protons and carbons on the molecules involved in this preparation. In the dicyclopentadiene compound, the signals at high field, 1.2–1.4 ppm, correspond to an AB system, protons labeled as 10, see Figure 1, originated by the anisotropic cone of the double bond under one of them ($^2J_{\text{AB}} = 7.9$ Hz; $^3J_{10,(7,1)} = 1.5$ Hz). At 1.54 and 2.11 ppm appears proton 5 (ddd $^2J_{\text{AB}} = 17.3$ Hz; $^3J_{5,6} = 9.5$ Hz for lowest field proton and $^3J_{5,6} = 2.0$ Hz for highest field proton). This separation is also due to anisotropic cone originated by double bond and disappears when the double bond is hydrogenated. The signal at 2.65 ppm (proton 6) appears as a doublet doublet of a pseudo triplet ($^3J_{6,5} = 9.5$ Hz and 2.0 Hz) with two coupling constants caused by a different dihedral angle,⁸ the other coupling constants are similar ($J_{2,7} \approx 2.0$ Hz). The signals at 2.71, 2.80 and 3.14 ppm (protons 1, 7 and 2, respectively) are most complicated to elucidate the coupling constants. The olefinic protons behave as an AB system and appear at 5.41 ppm (protons 3 and 4) and 5.88 ppm (protons 8 and 9). The assignment was done with the aid of HMBC and HSQC techniques. With the signals of dicyclopentadiene, the derived compounds were assigned and are very easily correlated. The identification via NMR of the chemically transformed derivatives is straightforward.

3. Experimental

^1H and ^{13}C NMR spectra were recorded on a Bruker AC-400 or on a Bruker AC-200P with CDCl_3 as a solvent. Chemical shifts are reported in ppm relative to TMS. *N*-Bromosuccinimide, NBS, was recrystallized prior to use⁹ and quinoline was distilled prior to use.⁹ Dicyclopentadiene, ethanol, and chloroform were used without any purification. The numbering of protons and carbons is indicated in Figure 1.

3.1. Preparation of tricyclo[5.2.1.0^{2,6}]dec-3-ene (8,9-dihydrodicyclopentadiene)

Nickel acetate (1.5 g, 6.0 mmol) and NaBH₄ (6.0 mL, 6.0 mmol, 1.0 M in ethanol) were added in a hydrogenation bottle and were left stable until the evolution of hydrogen was ceased. Then, dicyclopentadiene (30.0 g, 227 mmol in 50.0 mL of ethanol) was added. The flask was connected to a Parr hydrogenator apparatus and purged with hydrogen three times. The Parr apparatus was filled with hydrogen until 40 psi of pressure and the mixture was stirred until 10% of hydrogen in excess was consumed. The mixture was filtered over Celite and was then cooled and filtered to separate a white solid. This procedure was repeated three times. Yield 66–75 g (77% at average). ¹H NMR (CDCl₃, 200 MHz) δ ppm: 1.23–1.24 (m, CH₂(8,9), 4H), 1.44 (q, CH₂(10), 2H), 2.12 (s, CH, 1H), 2.19–2.29 (m, H(5,7,1) 3H), 2.53 (m, H(6) 1H), 2.99 (m, H(2), 1H), 5.60 (m, CH(3,4), 2H). ¹³C NMR (CDCl₃, 50 MHz) δ ppm: 22.39 and 25.63 (CH₂(8,9)), 32.64 (CH₂(5)), 39.95 and 41.37 (CH(7,1)), 41.55 (CH₂(10)), 41.96 (CH(6)), 53.34 (CH(2)), 130.75 and 133.31 (CH(3,4)).

3.2. Preparation of 5-bromotricyclo[5.2.1.0^{2,6}]dec-3-ene (5-bromo-8,9-dihydrodicyclopentadiene)

8,9-Dihydrodicyclopentadiene (5.0 g, 37.3 mmol) and NBS (6.6 g, 37.1 mmol) were dissolved in CCl₄ (30 mL) and added to a round-bottom flask fitted with a refrigerant, a stirrer and inert atmosphere, this system was refluxed for 4 h. At the end, the solid formed was filtered and the solvent was evaporated. The resulting liquid was passed through a column with silica gel using chloroform as an eluent. An oily yellow liquid was separated. Yield 5.3 g (*d* = 1.32 g/mL, 67%). ¹H NMR (CDCl₃, 200 MHz) δ ppm: 1.00–1.15 (m, H(8,9) 4H), 1.16–1.60 (m, H(10) 2H), 2.3 (s wide, H(5,7,1) 3H), 2.96 (m, H(6), 1H), 3.22 (m, H(2), 1 H), 5.90 (s, H(3,4), 2H). ¹³C NMR (CDCl₃, 50 MHz) δ ppm: 22.33 and 25.14 (CH₂(8,9)); 39.48 and 40.10 (CH(7,1)), 40.14 (CH(6)), 41.18 (CH(10)), 51.79 (CH(2)) 58.13 (CH(5)); 133.16 and 139.29 (CH(3,4)).

3.3. Preparation of tricyclo[5.2.1.0^{2,6}]deca-2,4-diene (isodicyclopentadiene)

5-Bromo-8,9-dihydrodicyclopentadiene (5.32 g, 25.0 mmol) and quinoline (4.67 g, 36 mmol) were added in a round-bottom flask fitted with a distillation apparatus. The system was heated until 105 °C and at 20 mmHg. The reaction was carried out until distilled liquid stopped. The ¹H NMR of the resulting liquid was similar to the reported isodicyclopentadiene.³

4. Conclusions

The title compound, isodicyclopentadiene, was prepared by an alternate route and 5-bromo-8,9-dihydrodicyclo-

pentadiene was prepared for the first time and fully characterized by NMR spectroscopy. The assignments of dicyclopentadiene were done in an attempt to characterize this new brominated compound. This new preparative synthesis is more easy and direct than the route reported by Katz.

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