

Symmetrically tetra substituted cyclooctatetraene derivatives. Diels Alder reactions of 3,4,7,8-tetrakis-exo-methylenecycloocta-1,5-diene and bis-furano COT derivative.

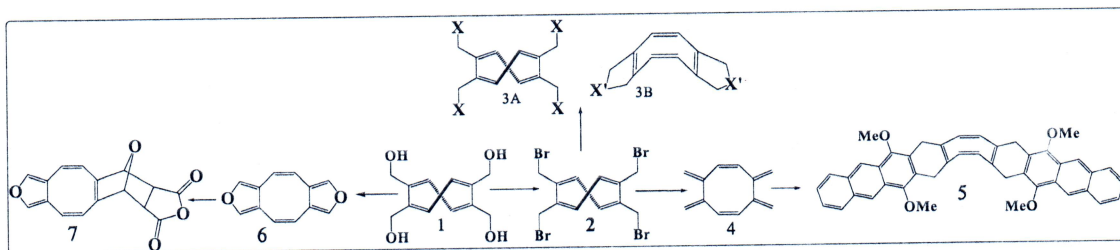
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Time:3.30pm-4.30pm

Abstract

1,3,5,7- Cyclooctatetraene [COT] or [8]annulene is a fascinating molecule, it was synthesised in 1911.¹ It exists in tub confirmation which undergoes rapid tub to tub ring inversion and π -bond shift isomerization. COT been has used as ligand for d and f-block metals in organic synthesis.² Symmetrically tetra substituted COT molecules are either C_{2v} or D_2 symmetric molecules and having different physical, chemical and spectroscopical properties.³ Flapping molecules have flexible COT ring at the centre with rigid polyarene wings and they have served as multifunctional materials in the field of organic photonics and electronics.⁴ COT and its derivatives were synthesized by Ni(0) catalysed cyclotramerization of acetylene and its derivatives.⁵

In this seminar, synthesis of D_2 symmetric 1,4,5,8-tetrakis(CH_2X)cycloocta-1,3,5,7-tetraenes (**3A**) and C_{2v} symmetric COT derivatives in which five membered ring is fused to the COT ring(**3B**),⁶ will be discussed. A novel synthesis of V-shaped COT fused acenes (**5**) by Diels-Alder cycloaddition of 3,4,7,8-tetrakis-exo-methylenecycloocta-1,5-diene(**4**) with various dienophiles,⁷ will also be discussed. A better synthetic method for bis furan (**6**) which is an antiaromatic COT derivative and its Diels-Alder reaction to monoadducts (**7**) will be discussed.(**scheme 1**).



Scheme 1: Synthesis of symmetrically substituted COT derivatives.

1. R. Willstätter, E. Waser, *Chem. Ber.*, **1911**, *44*, 3423–3445.
2. a) K. W. Glaeski and W. A. Donaldson, *Mini-Rev. Org. Chem.*, **2012**, *9*, 31–45; b) P. W. Roesky, *Eur. J. Inorg. Chem.* **2001**, 1653–1660.
3. (a) L. A. Paquette, *Acc. Chem. Res.*, 1993, *26*, 57–62; (b) K. Trindle and T. Wolfskill, *J. Org. Chem.*, **1991**, *56*, 5426–5436.
4. T. Yamakoda, S. Takahashi, K. Watanabe, Y. Matsumoto, A. Osuka and S. Saito, *Angew. Chem., Int. Ed.*, **2018**, *57*, 5438–5443.
5. a) W. Reppe, O. Schlichting, K. Klager and T. Toepel, *Justus Liebigs Ann. Chem.*, 1948, 560, 1–92; b) P. A. Wender and J. P. Christy, *J. Am. Chem. Soc.*, **2007**, *129*, 13402–13403; c) T. R. Boussie and A. Streitwieser, *J. Org. Chem.*, **1993**, *58*, 2377–2380.
6. S. Gadigennavar, M. Ranganathan and S. Sankararaman, *Org. Biomol. Chem.*, **2020**, *18*, 9284–9291.
7. S. Gadigennavar and S. Sankararaman, *Org. Biomol. Chem.*, **2020**, *18*, 6738–6744.

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Guide Signature