Review on synthetic approaches for donor - acceptor conjugated molecules.

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Abstract

Organic molecules containing both an electron-donating group (donor) and an electron-withdrawing group (acceptor) at opposite ends of a conjugated pi-electron system (often referred to as push– pull systems) are of fundamental importance in materials chemistry since they serve as critical components for many advanced technologies. In this regard many synthetic approaches have been applied in order to achieve an efficient donor – acceptor system. Some of the efficient methods for preparation of push –pull system has been discussed along with the yields of resultant.

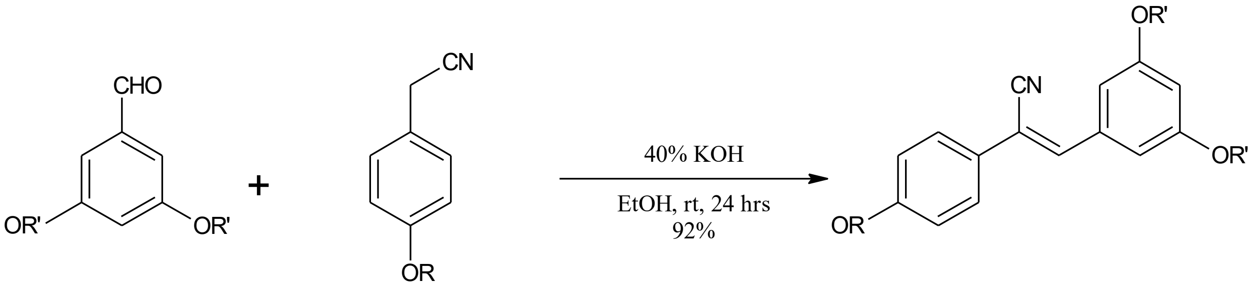
Introduction

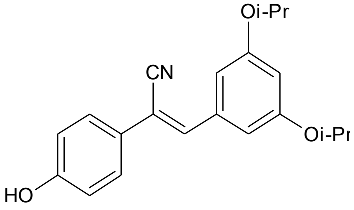
Organic molecules containing both an electron-donating group (donor) and an electron-withdrawing group (acceptor) at opposite ends of a conjugated p-electron system (often referred to as push– pull systems) are of fundamental importance in materials chemistry since they serve as critical components for many advanced technologies.

The common method to adjust LUMO , HOMO, and band gap of conjugated molecules by taking electron donor and acceptor groups is , that the hybridization between the HOMO of the donor and the LUMO of acceptor produces a relatively narrow band gap. Thus various methods have been tried for the synthesis of these type of push-pull systems.

Synthetic approaches for donor acceptor conjugated molecules :

A series of Donor-Acceptor conjugated molecules were synthesized and characterized to determine the effect of electron-donating and withdrawing strengths and investigation of optical properties. The most common class of conjugated molecules containing (Z)-cyano resveratrol analogues a, b, and c has been reported by condensation of the appropriate aldehyde with the appropriate 2-phenylacetonitrile[1].





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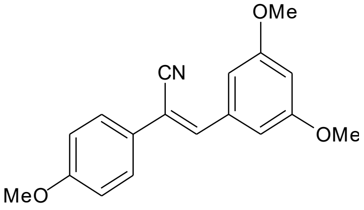

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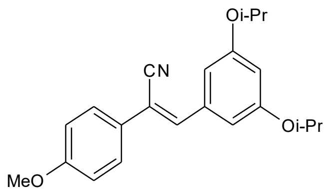
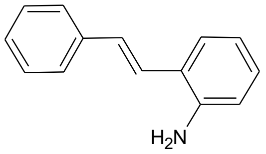


(c)

Donor-acceptor oligophenylenevinylenes (OPVs) bearing an electron-donating 2-(2-butoxyethoxy) ethoxy group at one end and various electron-withdrawing groups including alkylsulfonyl, cyano, and nitro functionalities at the other end have been synthesized with good yield using Wadsworth-Emmon reaction routes.[2]

Another class of conjugated molecule (E)-Aminostilbene(a,b,c) has been reported by the Wittig route[3]. An appropriate molecule of ortho-, meta-,paranitrobenzaldehydes reacted with triphenylphosphonium chloride in CH_2Cl_2-H_2O.The trans isomer so produced was purified by recrystallisation and gave pale yellow solid with a yield of 40%. Reduction of nitro group to amino by Zn/HCl-AcOH as reducing agent to give yield of 85%, its purification yield was 98.5%.[4]



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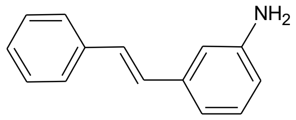

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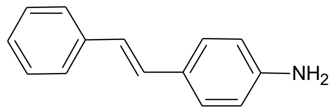
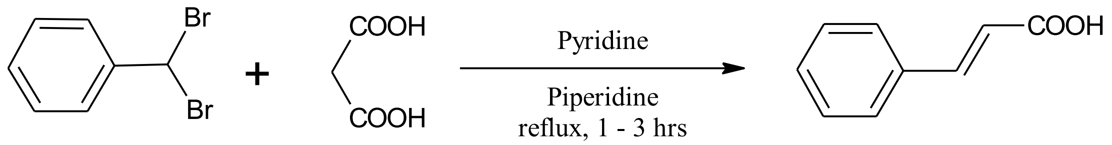
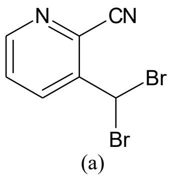


(c)

Synthesis of α, β-unsaturated carboxylic acids from gem-dibromomethylarenes was reported by a Knoevenagel-Doebner reaction. In this benzal bromide was treated with malonic acid in presence of pyridine to produce α,β-unsaturated carboxylic acid which is cinnamic acid with a good yield of 93% as a white solid.

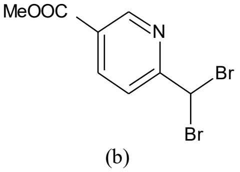


This reaction provides α, β-unsaturated carboxylic acid in single step therefore has a wide application in synthetic chemistry. Various substituted gem-dibromomethylarenes (a,b,c) were reacted in same manner to produce a good yield of α,β-unsaturated carboxylic acids.[5]



(a)

(gave yield: 94%)



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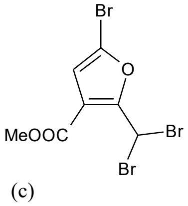
(gave yield: 92%)

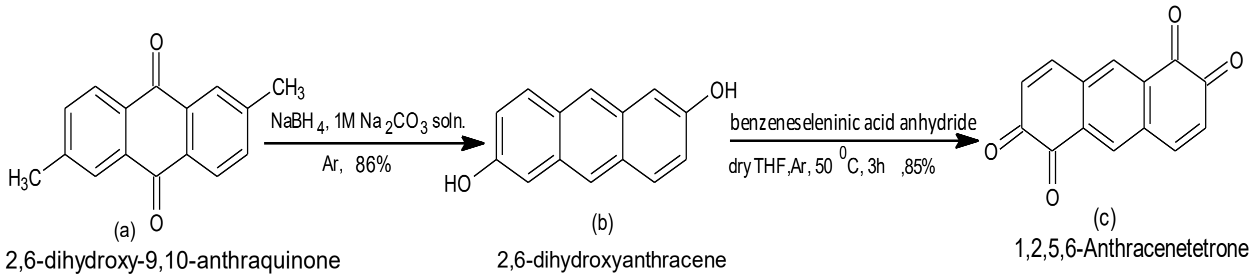


(c)

(gave yield: 91%)

1,2,5,6-anthracenetetrone was synthesized by adding 2,6- dihydroxyanthracene in 25mL dry THF purged with Ar to a solution of benzeneseleninic acid anhydride in 50mL dry THF under argon. The reaction was heated to 50^0C for 3h and then allowed to cool to room temperature.

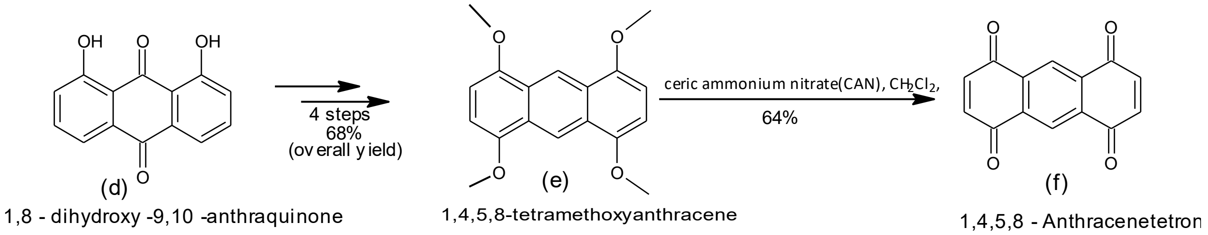
After storing reaction overnight, solvent and volatile by-products were removed in vacuo using rotary evaporator. Inhalation of selenium by- products was prevented by placing the reaction in fume hood. Resulting solid from 1,4-dioxane gave red needles (1,4- dioxane solvates) is then recrystalized and dried to get pure tetrone (c) with yield of 85%.[6]



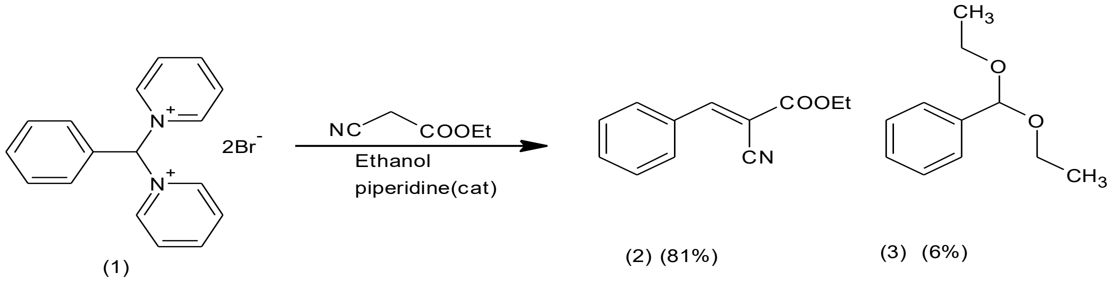
Here are some results obtained: 1H NMR (600MHz, THF-d8): δ= 8.10 (s, 2H), 7.64 (d, J= 10.2Hz, 2H), 6.44 (d, J= 10.2Hz, 2H) ppm (in accordance with the literature [7].

1,4,5,8-anthracenetetrone molecule was reported and was synthesized by addition of solution of Ceric ammonium nitrate (CAN) in 6mL H_2O dropwise to 13g silica in 100mL round-bottom flask. The solid was stirred until a free-flowing yellow solid was obtained, 25mL of CH_2Cl_2 was then added, followed by the addition of 1,4,5,8-tetramethoxyanthracene(e). Another 10mL CH2Cl2 was used to transfer residues of (e). The reaction stirred and then filtered through sintered glass funnel to remove silica. The silica was washed with 200mL CH_2Cl_2 and the combined solutions were washed with water and dried over Na_2SO_4.

The solvent was removed in vacuo and the solid residue was recrystallized from 1,4-dioxane, which afforded red needles (1,4-dioxane solvates). After drying, tetrone (f) was obtained in yields of 64%.1H NMR (600MHz, $CDCl_3$): δ= 8.82 (s, 2H), 7.14 (s, 4H) ppm (in accordance with the literature apart from reversed integrals[8]. 13C NMR (151MHz, $CDCl_3$): δ =183.3 (C), 139.4 (CH), 135.1 (C), 125.8 (CH) ppm

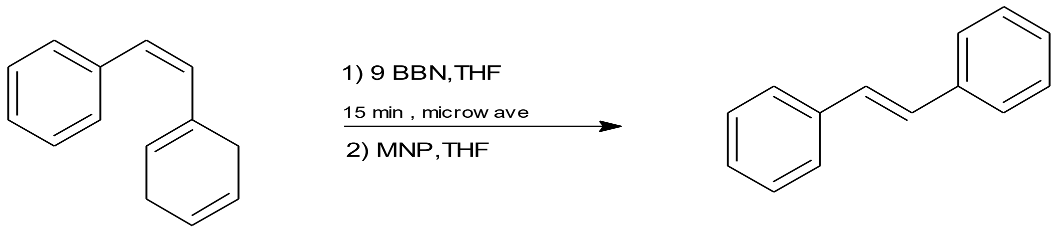


Benzaldehyde diethylacetal was prepared by the condensation of benzylpyridinium salts with active methylene compounds in the presence of base was reported. The reaction was further probed by isolating the bis-pyridinium salt of benzal bromide (1). On treating this intermediate with ethyl cyanoacetate in absolute ethanol containing a catalytic amount of piperidine at reflux for 4 h, ethyl-2-cyano-3-phenylacrylate (2) was obtained in 81% yield. Benzaldehyde diethylacetal (3) resulting from the reaction between ethanol and the bis-cation was also isolated in small quantity.[9]



Another class of conjugated molecule have been created by hydroboration–elimination route to synthesise E -stilbenes. Cis stilbene was treated with 9 BBN in presence of THF for 15 min in microwave radiations and was then treated with MNP in presence of THF. The isomerization was 61% complete at 75°C whereas at 125 °C the isomerization was essentially complete[10]

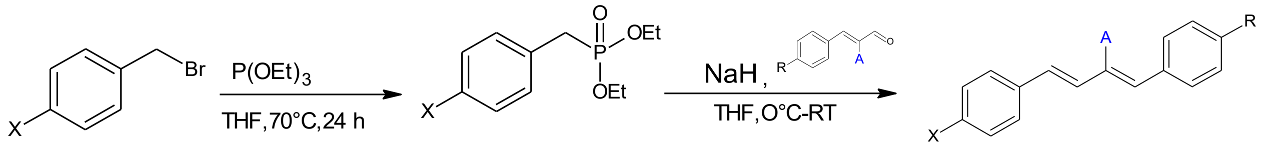
Stilbenes and their derivative are used as precursors for synthesis of other compounds. They exhibits useful properties and are widely used in field of medicinal,optics, and chemotherapy [11].



Also derivatives of Diphenylbutadiene and its analogus (a , b , c) were reported by Horner–Wadsworth–Emmons reaction [12] with about 35-60% yield. Triethylphopsphite was added to THF solution of benzylbromide solution. This solution was refluxed in inert atmosphere. The reaction mixture was cooled to room temperature and further cooled down at 0°C in ice bath.

Further sodium hydride was added to the reaction mixture was under continuous stirring for about 5 min, then aldehyde was added to the above part dropwise with stirring for about 30 min.

Light induced isomerization of alkenes and polyenes is very important for many chemical and biological reaction , chemically active pigments such as the opsin family of proteins reflects varied application in biological and materials[13,14]. Photoisomerization of 1,4-diphenylbutadiene and its derivative results in corresponding cis–trans and trans–cis isomers [15]. The nitro substituted diphenylbutadienes compounds showed remarkable solvatochromism due to the presence of strong intramolecular charge transfer (ICT) states[16,17].

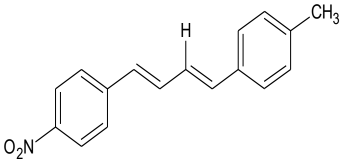


$X=NO_2,H,CN$

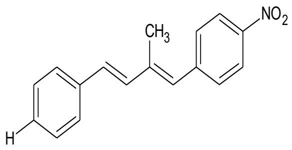
$R= NO_2,CH_3,H$ a. $X=H,A=H,R=NO_2$

$A=CH_3,H$ b. $X=NO_2,A=H,R=CH_3$

c. $X=H,A=CH_3,R=NO_2$



(a)



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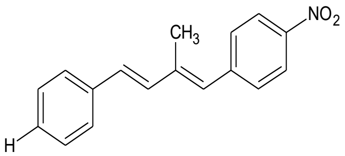

(c)

Conclusion

From above it is concluded that donor-acceptor conjugated systems and can be synthesized by various different reactions such as wittig reaction, knoevengel-doebner reaction, condensation reaction,wadsworth-emmon reaction and hydroboration-elimination reaction. It was found that wittig route produces maximum yield followed by knoevengel-doebner reaction.

These donor- acceptor conjugated systems have great importance in biological processes such as anti-microbial, anti-fungal and anti-bacterial activities along with various applications in industrial processes.

Acknowledgement

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