Research Article

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Journal of Structural Chemistry & Crystallography Communication

2020
Vol. 6 Iss. 2

A Facile and Commodius method for the Synthesis of 1,8-dihydro-as-indacene

Abstract

IThe synthesis of 1,8-dihydro-as-indacene was prepared in 8 steps starting from alkylation of 2-methyl-furan with formaldehyde and substituted with ethylamine hydrochloride to gives a isolated mixture of 5-methyl-2-furfuryldimethylamine, the amine was quaternized by treating with methyl iodide and anion exchange using Ag2O resulted in the intermediate ammonium hydroxide subsequently without isolation, to removing the water by hydrolysis process. The hydroxide was pyrolyzed by a transformation of furanocyclophane (4a). Photooxidation of the 4a in methanol gives a mixture of oxy diketone (5a) and a peroxidic compound, either a methoxy diketone. Sodium iodide in acetic acid reduces the peroxide to give pure 5a, which is dehydrated by sodium carbonate to (6a) and a purified the diketone in column chromatographic method to gave a pure 6a. sodium borohydride reduction, acetylation(7a) and pyrolysis yield dihydro-as-indacene (8a).

Received: June 20, 2020; **Accepted:** July 02, 2020; **Published:** July 27, 2020

Introduction

The strong electronic interaction between the two metal centers in organometallic complexes make them potential model systems for organometallic polymers, which might result in a range of interesting electronic, magnetic and optical properties, as well as useful in homogeneous catalysis due to the homogeneous catalysis due to the presence of cooperative effects3.

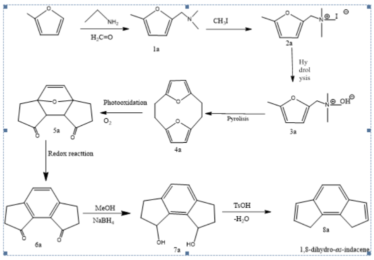
The introduction of s-indacene and as-indacene belong to a class of conjugated hydrocarbons characterized by having 4nπ system. A suitable developer to access these type of material is the introduction of organometallic units, such as a oligomers or polymers. due to there high structural diversity and architectonic flexibility, owing to the versatility and different states of the redox centers. This, in conjugation with the variability of the metal environment can be tuned employing different kinds of substituents and ligands.9-10 one of the requirements to achieve a conducting organometallic polymer, is that the spacer ligand bearing different redox centers must be suitable to favour the electronic communication between those redox centers.

The saturation of substituent electronic effects has been a subject of much concern partly because of the failure finding systems and experimental methods sufficiently sensitive to probe the proposed effects. So far the convincing support for the concept of conjugated systems having π-electron acceptor or donor groups while the importance of polar saturation effects has been assumed to be minor.1 In this matter, fused delocalized polycyclic bridge ligands, such as binuclear complexes of pentalene,s-indacene and as-indacene, are particularly effective to promote the interaction between different redox centers due to geometry, rigidity, and electron rich π systems. The main difficulty to attain organometallic polymers, is the decrease in solubility as the number of organometallic units increases.It has been postulated that the inclusion of alkyl substituents in the spacer ligands can be increase the solubility of the synthesized complexes.23 As it has been demonstrated by our research group, the feasibility of s-indacene to be mono, or bi-deprotonated selectively is a useful strategy in the development of a rational synthetic stage route, which allows the preparation of heterobimetallic and oligomeric complexes.2,5,34

The use of enantiomerically pure indane derivatives as ligand as been extensively described in literature, Where as reports of ligands based on 1,2,3,6,7,8-hexahydro-as-indacene are scares.10 Nevertheless, rigid 1,8-disubstituted as-hydrindacenes can become the cornerstone of an interesting new ligand architecture. In order to investigate the applicability of such structures in asymmetric synthesis, we needed to have facile access to I,8-dihydro-as-indacene.

The synthesis of as-indacene was previously long ago, by Hafner, Katz, Erden , and Bell 11,12,19,21 but these synthesis are relatively tedious or lead to the formation of a as-indacene isomers. It is for this reason that we decided to explore an alternative and facile synthetic route for the synthesis of 1,8-dihydro-as-indacene in 8 steps, that allows an improvement in the synthesis and yield of the described isomer of this important ligand.

Schematic representation:



Discussion of Schematic representations:

The catalytic alkylation of methylated group, which was obtained in two easy steps from 2-methyl-furan with formaldehyde and substituted with dimethylamine hydrochloride was treated with gives to a isolated mixture of 5-methyl-2-furfuryldimethylamine in a very good yield (1a). The amine was quaternized by treating with methyl iodide to gave a tri methyl furan (2a). And anion exchange using Ag_2O resulted in the intermediate ammonium hydroxide subsequently without isolation, to removing the water by hydrolysis process to gives a 3a, was good yield and this Is a hydroscopic product. The hydroxide was pyrolyzed by a transformation of furanocyclophane 4a. For the synthesis use was made of the discovery by Wasserman and Doumaux that photooxidation of the readily preparable furanocyclophane 4a yields the oxy diketone 5a, a reaction that appears to occur through the intermolecular Diels-Alder condensation of the diene.

A number of changes in procedure made the reaction more efficient for use in a multistep synthesis. Among these was a change of solvent from ethanol to methanol because the scale on which the reaction can be run limited by the solubility of the furanocyclophane , which is greater in methanol. In this solvent, with methylene blue as the photosensitizer, 1mol of oxygen was observed upon irradiation, but only small amounts of the oxy diketone 5a crystallized when the reaction mixture was concentrated and cooled. Significant amounts of an impurity were present.

In either case reduction with sodium iodide in acetic acid should give the oxy diketone 5a, verified when the solid reaction product of the photooxidation was treated with these reagents, Iodine was liberated and pure oxy diketone 5a resulted in good yield. Since brief exposure of this compound to sodium carbonate solution results in its dehydration to 1,8-dioxo-2,3,6,7-tetrahydro-as-indacene 6a, resulted in a pure and good yellow coloured yield was formed.

Sodium borohydride and methanol reduction of the diketone 6a yields the diols 7a, mixture (approximately meso 3/1) of cis and trans isomers. Although this mixture was not separated, the individual isomers could be isolated by fractional crystallization and each acetylated or extracted with ethyl acetate and washed with sodium chloride dried sodium thiosulphate and dried with vacuo to gave a yellow coloured diols 7a, the diols was dissolved in dry benzene and p-TAS.H_2O was added. The mixture was subsequently refluxed in a Dean-Stark apparatus. Was dissolve in hexane purified the column chromatography to finally gave a good purified yellow colour solid crystals of 1,8-dihydro-as-indacene 8a, was formed.

The 1,8-dihydro-as-indacense are soluble in most organic solvents. However, substitution by ethyl groups increased the solubility greatly, making these new ligand suitable as starting materials for organometallic polymers. To use these new ligands as spacers in organometallic polymers. It is very important to find the best conditions to make the monoanions and the corresponding dianions.

`Experimental Section

(1a) N,N-dimethyl-1-(5-methylfuran-2-yl)methanamine.

Procedure. - The details of the reaction of 2-methyl-furan with formaldehyde and ethylamine hydrochloride will illustrate the general procedure followed.

(A) To a solution of 163 g. (2 moles) of ethylamine hydrochloride in 162 g. of 37% formaldehyde (2 moles) at 30 ° in a round bottom flask equipped with a dropping funnel, stirrer and reflux condenser,82 g. (1 mole) of 2-methylfuran was added drop wise during four hour. Stirring was continued until heat evolution ceased. The mixture was cooled to room temperature and neutralized with 81 g. of sodium hydroxide dissolved in 160 cc. of water. The top organic layer was separated and the water solution extracted one with 300 cc. of ether. The combined ether and amine layer was washed with two 150 cc. portions of water and dried over sodium sulfate.

The ether was removed under the rotary evaporator, and the residue distilled (distillation process) under reduced pressure, Finally Distillation of the product gave 70 g. of colorless oil, b.p.71° to 78° (17mm), mp 133°c to 135°c yield, 70 g. or 48.9 % over-all yield from N,N-dimethyl-1-(5-methylfuran-2-yl) methanamine.($C_8H_{13}NO$):

(2a) N,N,N-dimethyl-1-(5-methylfuran-2-yl)methenamine Iodide

Procedure. - The details of the reaction of N,N-dimethyl-1-(5-methylfuran-2-yl)methenamine. with ether and iodomethane will illustrated the general procedure followed.

(B) The resulting of N, N-dimethyl-1-(5-methylfuran-2-yl) methenamine (70 g in 250 ml. of ether) , to transfer a 1L of round bottom flask to stirring 30 min, after add a 96 g. of methyl iodide to stirring at over- night under the nitrogen and maintained 0º C. Finally we get white precipitate was formed after filtration to collect the 160 g. of white solid N,N,N-dimethyl-1-(5-methylfuran-2-yl)methenamine powder. Percentage of yield was 88 %, MP 120-122°c.($C_9H_{16}NO+I$):

(3a)N,N,N-dimethyl-1-(5-methylfuran-2-yl) methenaminehydroxide (Hydrolysis process).

The after continue this process, the iodide (N,N,N-dimethyl-1-(5-methylfuran-2-yl)methenamine Iodide), was converted in to the hydroxide 160 g in trimethyl was treating with 250 mil of water with 81 g of silver oxide, and stirring with 2-3 hrs. and next filtration, washing the precipitated silver iodide, and removing the water either by distillation at 30° (0.1 mm) or by lyophilization. This product was hydroscopic so you dried to constant weight in a vacuum desicator over P_2O_5. The yield was 66 g. (63%) mp 162-

164°c($C_9H_{17}NO_2$):

(4a) furancyclophane (pyrolyzed process).

The hydroxide (N,N,N-dimethyl-1-(5-methylfuran-2-yl) methenamine hydroxide) 66 g was pyrolyzed by heating it in oil bath at 150-155° (0.2 mm). This product was volatile product so were trapped in 50 ml of ethanol containing 0.60 g of hydroquinone to stirring at 2-3 hrs to completely evaporate this product, again you have taken this only cooling product to start the reflux process in 2 hrs stirring at 80°c. (important wash with trapes to alcohol we get yellow color liquid was formed after you have keep this sample to refrigerator 1hr. after you have filtrate this sample to get collet the 4a.) after filtration with buchner funnel to collect the furanocyclophane white precipitate product and recrystallized from methylene chloride. The yield was 13 g (55%) mp 191°-192°c.($C_{12}H_{12}O_2$):

Photooxidation of furanocyclophane (5a).

As much as 10 g of 4a could be photo oxidized in 2 l, of methanol, but earlier experiments used only 5 g. The furanocyclophane 4a (5 g ,0.026 mol) in 1000 ml of methanol containing 0.65 mg of methylene blue was irradiated with a 650-W Sylvania sun-gun movie lamp (cooled by a flow of compressed air) oxygen was pumped through the solution from a gas buret by means of a circulating pump. The required amount of oxygen (1000 ml) was consumed in about 2 hr.

After the solution was concentrated on a rotary evaporator to 250 ml and half was stirred with 10 g of potassium iodide in 12 ml of water and 4 ml of acetic acid stirring at 2 hr after you added sodium thiosulphate until the iodine color disappeared. and next added sodium carbonate 10 g in 15 ml water 30 min stirring was added to neutralize the acid, and then another 100 ml of saturated sodium carbonate was added in the course of 30 min to catalyze the dehydration. the mixture as stirrer for 1 hr. after complete reaction to added 150 ml of water, and the solution was extracted four times with chloroform (200 ml). After draying (Na_2SO_4), filtration, and evaporation of solvent gave 4.2 g of a blue color solid oxy diketone (5a) was formed this means dehydration was failed. (you have to try only redox reaction process) and important solid blue color oxy diketone was formed the product so blue color solid means in our product it's not a pure compound so first you have to remove the methylene blue color so you have to use simple chromatographic techniques after gave the pure brown solid oxy diketone was formed. (4.2 g in 92% of yield), MP 179° to 180°c. ($C_{12}H_{12}O_3$):

Diketone (Redox reaction) (6a).

The resulting oxy diketone (5a) treating a solution of 4.2 g (0.019) in 100 ml methanol and saturated solution of 20 g Na_2CO_3 in 150 ml of water was added to catalyze the dehydration the mixture was stirred for 2 to 3 hrs. water (150 ml) was added and the solution was extracted four times with chloroform (250 ml). drying the (Na_2SO_4), filtration and evaporation of solvent gave 4g (88%) of a pale yellow solid diketone. The nmr spectrum of the material differed little from that of the recrystallized compound, melting point 206°-207°c). This compound was sublimized at 210°c.

And another method you also used purified the impure solid diketone by column chromatography method. This sample was dissolved ethyl acetate/hexane and purified by chromatography on silica gel (300ml, eluent: Ethyl acetate/EtOAc) resulting in 4.0 g of 6a (0.0214 mol, 88%) as a pale yellow solid diketone (208° to 210°).($C_{12}H_{12}O_2$):

Preparation of 1,8-diol-1,2,3,6,7,8-hexahydro-as-indacene (7a).

The details of the reaction of diketone with MeOH and $NaBH_4$ will illustrated the general procedure followed.

A suspension of diketone 6a (4.o g of 0.021 mol) was stirred in MeOH (119 ml) at 0° C, and $NaBH_4$ was added (0.81g,0.021mol) in several portion in such a way that the temperature did not exceed 10°c. The mixture was then stirred at room temperature for 2hr, after which it was poured into H_2O (300 ml) and EtOAc (320 ml). The aqueous layer was separated and again extracted with Ethyl acetate (480ml). The organic layer was washed with saturated aqueous sodium chloride and dried with sodium thiosulphate (Na_2SO_4). Filtration and removal of the solvent in vacuo resulted in 4.12 g (0.0216 mol,99%) as a (7a) yellow solid isomer (melting point at 110 to 111°c). ($C_{12}H_{14}O_2$):

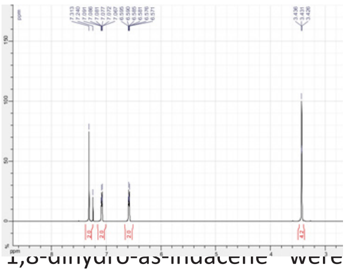
The Dihydro-as-indacene (8a).

The mixture of 7a (4.12 g, 0.0216 mol) was dissolved in dry benzene (400 ml), and after the mixture was heated at 80°c, p-TSA·H_2O was added (51mg, 0.268mol). The mixture was subsequently refluxed in a Dean-Stark apparatus for 180 min, cooled to room temperature, and poured in to 5% of aqueous $NaHCO_3$ (160 ml) to separate the organic layer was dried with Na_2SO_4. The slightly yellow solid, obtained after filtration and removal of the volatiles, was dissolved in n-hexane/dichloromethane (2:1) and purified by chromatography on silica gel 120ml, eluent: n-hexane) resulting in 3.31 g of 8a (0.0214mol,99%) as a yellow solid crystal dihydro -as-indacene (melting point). Its infrared spectrum in KBr has a maximum at 891 to 2898 cm^{-1}

^1HNMR (400 MHz, $CDCl_3$): =7.31 (s, 2Harom), 6.58 (t,J=1.6 Hz, 2H, 2×CCHC), 3.38 (d,J= 1.5 Hz, 4H, 2×CCH2C), 2.64 (qd,J=7.20,1.5 Hz, 4H,2×CH2CH3), 1.34 (t,J= 7.5 Hz, 6H, 2×CH2CH3).

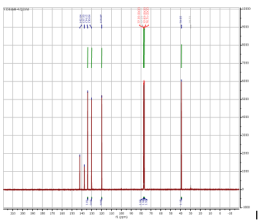
Anal. Calcd for $C_{12}H_{10}$: C, 93.46; H, 6.54. found: C, 93.67; H,6.71.

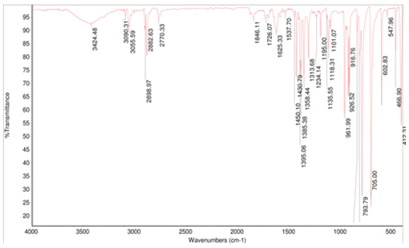
Discussion of Characterization:

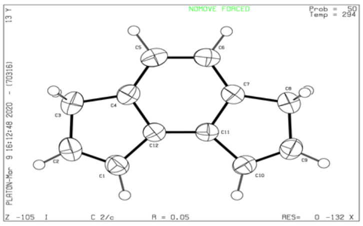


Monocrystal of 1,8-dihydro-as-indacene were obtained by solvent diffusion techniques.This fig shows the ctystalline struture analysis that the the compound I,8-dihydro-as-indacene crystallizes in a monoclinic space group C2/C, with molecule per unit cell

II).^{13}C NMR Spectrum of 1,8-dihyro-as-indacene.







Conclusion:

In conclusion, we have succeeded in developing a facile and commodius method for the Synthesis of 1,8-dihydro-as-indacene compounds. Finally, this synthesis was finished in around eight steps a new dihydro-as-indacene has been accomplished by considering 2-methyl furan with formaldehyde and various substituted ammonium chlorides. The structure of these compounds has been demonstrated in the instance by the identity of the properties and mixed melting point of the product with those of a sample prepared by an alternative and unambiguous method. This synthesis opens an easy access to possible new organometallic complexes binuclear metal synthesis, thus following the research line of our work.

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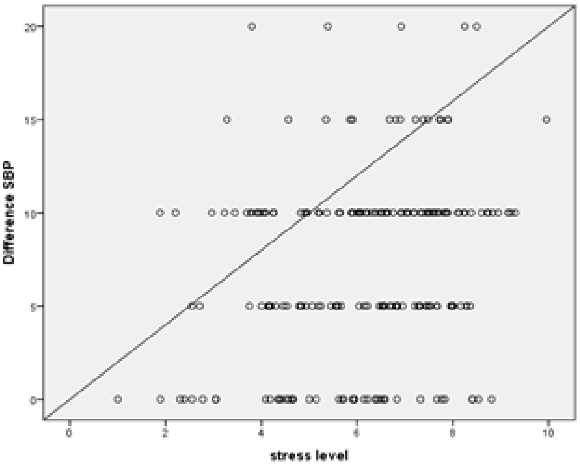

Figure 2: Effect of Occupational stress on changing systolic blood pressure