



SYNTHESIS OF SOME NEW 1, 3 DISUBSTITUTED NAPHTHALENES AND 1, 3, 7-TRISUBSTITUTED NAPHTHALENES BY THE REACTION OF BENZYL PYRIDINIUM BROMIDE AND 4- NITRO BENZYL PYRIDINIUM BROMIDE WITH α , β – UNSATURATED KETONES

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ARTICLE INFO

Published on: 15-09-2014
ISSN: 0975-8216

Keywords:

Disubstituted Naphthalenes,
Trisubstituted Naphthalenes,
Benzylpyridinium Bromide, 4-
Nitro Benzyl Pyridinium
Bromide, A,B-Unsaturated
Ketones

ABSTRACT

A series of new 1, 3- diarylnaphthalenes and 1, 3-diaryl-7-nitro naphthalene have been synthesized in quantitative yields by the interaction of benzylpyridinium bromide and 4- nitrobenzylpyridinium bromide with a wide range of substituted benzylideneacetophenone using anhydrous $AlCl_3$ or $ZnCl_2$ in a mixture of ammonium acetate in acetic acid cyclization agent, the structures of the products were established by NMR spectral data.

INTRODUCTION

Literature survey reveals that various methods for the synthesis of naphthalene derivatives involve several steps that affect the yield of the final products. The first attempt in this direction was made by House et al., who synthesized 1,8-diphenyl naphthalene by reaction of 8-phenyl octal-1-one with phenyl magnesium bromide to form an alcohol which undergo dehydro-halogenation and dehydration.

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The reaction of benzyl pyridine bromide and 4- nitro benzyl pyridine bromide with various substituted benzylidene acetophenones in the synthesis of a wide range of naphthalene derivatives ¹.

EXPERIMENT

Preparation of benzyl pyridinium bromide

Reagents were obtained from commercial sources i.e. BDH, Merck etc. Thus 4-nitrobenzyl bromide was prepared by the direct bromination. The substituted benzylidene acetophenones, benzylidene 2-acetothiophenes were prepared⁶. This method consists of stirring the equimolar quantities of aromatic aldehydes and methyl ketones in the presences of an alkali at 0°C. The resulting precipitate of α , β -unsaturated ketones was recrystallised from ethanol by benzene: petroleum ether (60°-80°C) in 40-80% yields.

A solution of pyridine (39.5g 50mmol) in anhydrous benzene was allowed to reflux on water both for 4 hours. A solid mass was precipitated which was filtered, dried and recrystallised twice from chloroform-n-hexane to give white shining crystals of benzyl pyridinium bromide in 81% yield, m.p 168-70° (m.p.170-72°C)⁶⁻⁸.

Anal. Data found: C-50.58, H-3.90%.

Calcd. For (C₁₂H₁₂Br N) C, 50.61, H, 3.86%.

Preparation of 4-nitrobenzylpyridinium bromide

A mixture containing (21.60 g 100 mmol) of 4-nitro-benzyl bromide and (7.9g 100 mmol) pyridine in 100 ml. of anhydrous benzene was heated on a water bath for 6-8 hrs. Excess of the solvent was evaporated and petroleum ether (60°-80°C) was added to precipitate 4-nitrobenzylpyridinium bromide. This salt was twice recrystallised from chloroforms-n-hexane in the ratio1:2 to give a pale yellow crystalline compound, m.p.220-22°C (M.P. 218.19°C), yield 26.5g (90%).

Anal. data found : C=48.5 , H, 3.70%

Calcd for C₁₂H₁₂Br N₂O₂C₁ 48.81 ,H,3.27%

H-NMR spectra (D.M.S.O) ppm 6.20(2H, N-CH₂), 6.85 -9.40 (m,9H, ArH).

IR spectra (KBr) max (Cm⁻¹) 3045(N-CH₂), 1515 (-NO₂).

Preparation of 1,3 diaryl – 7-nitronaphthalene

In a 100 ml round bottle flask, equipped with a reflux condenser and a magnetic stirrer, was placed a solution of 4-nitrobenzyl pyridinium bromide (0.88 g, 3 m.mol. in 5.0 ml of glacial acetic acid followed by the addition of 3.0 g anhydrous zinc chloride. The mixture was stirred at 200°C for 6-8 hours under an inert atmosphere of nitrogen. The resulting solution was allowed to stand overnight at room temperature, Ice cold water (20 ml) was then added. The precipitated solid so obtained, was filtered off, dried and chromatographic over neutral alumina chloroform fraction which on recrystallisation from an appropriate solvent gave a fine crystalline solid due to formation of 1,3 diaryl-7-nitronaphthalenes (16).

Preparation of 1, 3-diaryl 7-naphthalene by using General Procedure

A mixture of 4-chlorobenzylpyridinium bromide (0.85g, 3 mmol) and α , β -unsaturated ketones (3 mol) was stirred at 200°C in the presence of anhydrous zinc chloride (3.0g) in 10 ml glacial acetic acid for 6-9 hours under nitrogen. Reaction mixture, after keeping overnight at room temperature, was poured into mass was separated by filtration, dried and subjected to column chromatography using neutral alumina as absorbent and

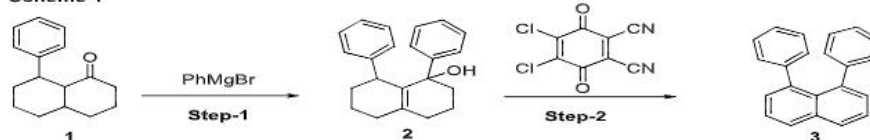
chloroform as eluent. The products were recrystallised from suitable solvents to give better yield of the title compound (17). The NMR spectral data of naphthalene 10.27 g 50 m.mol in ml. of anhydrous benzene was allowed to reflux on a water bath for 4 hours.

A solid mass was precipitated which was filtered, dried and recrystallised twice from chloroform: n-hexane to give 81% yield (11.50), m.p. 168-70°C).

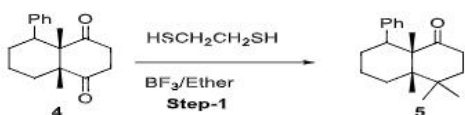
Anal. Data found : C,50.58,H,3.90%

Calcd. For $C_{12}H_{11}Br$ CL NC 50.61, H, 3.86%

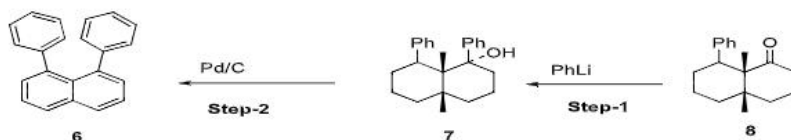
Scheme 1



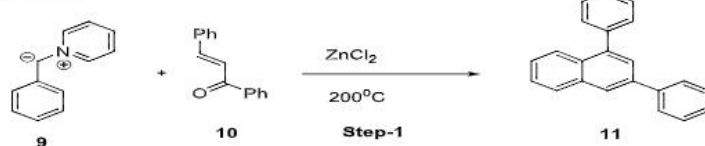
Scheme 2



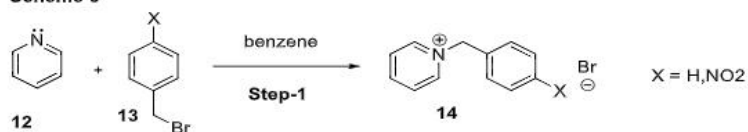
Scheme 3



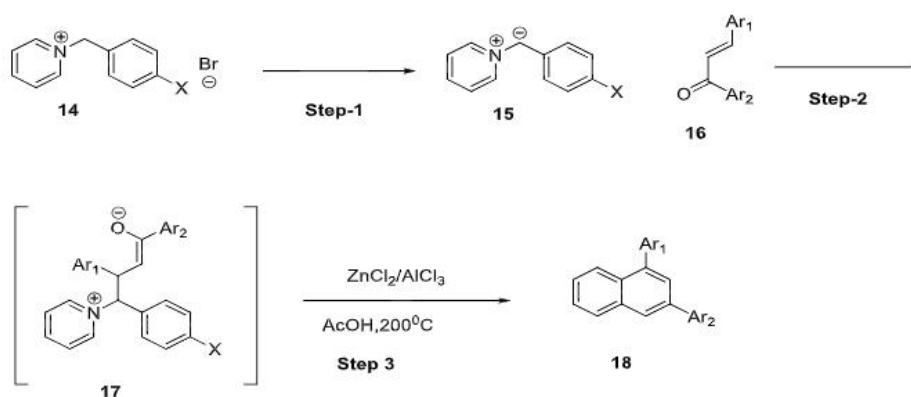
Scheme 4



Scheme 5



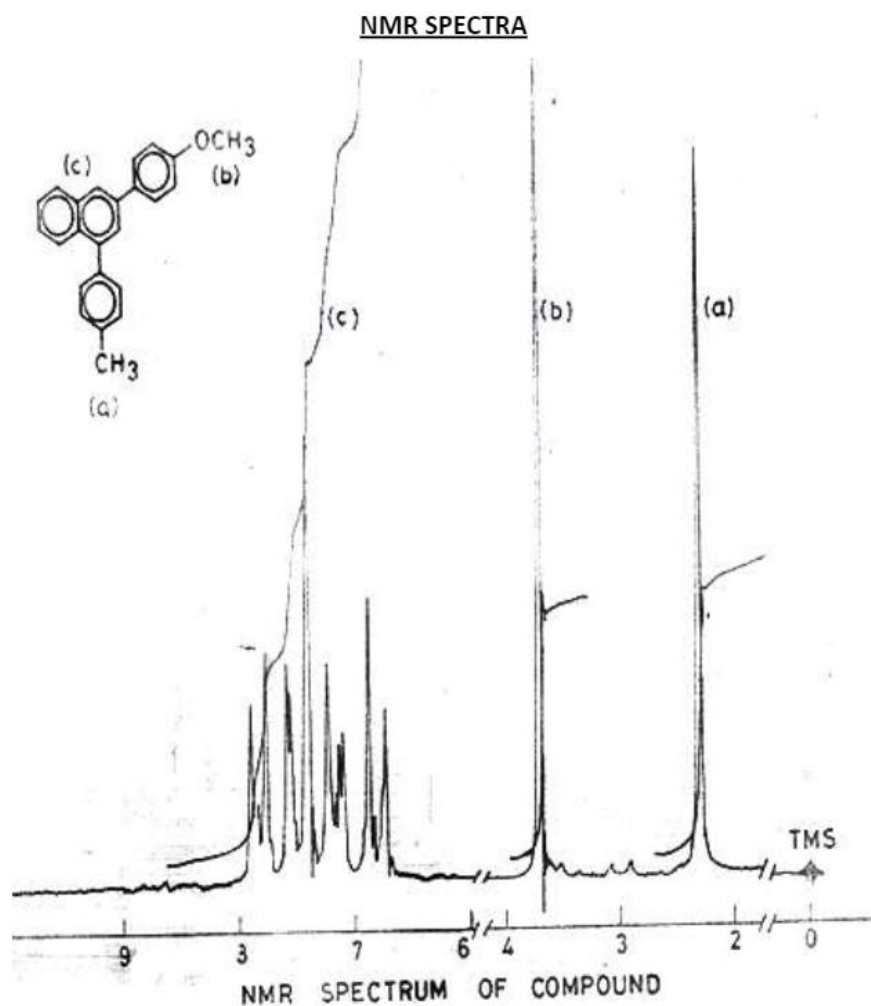
Scheme 6

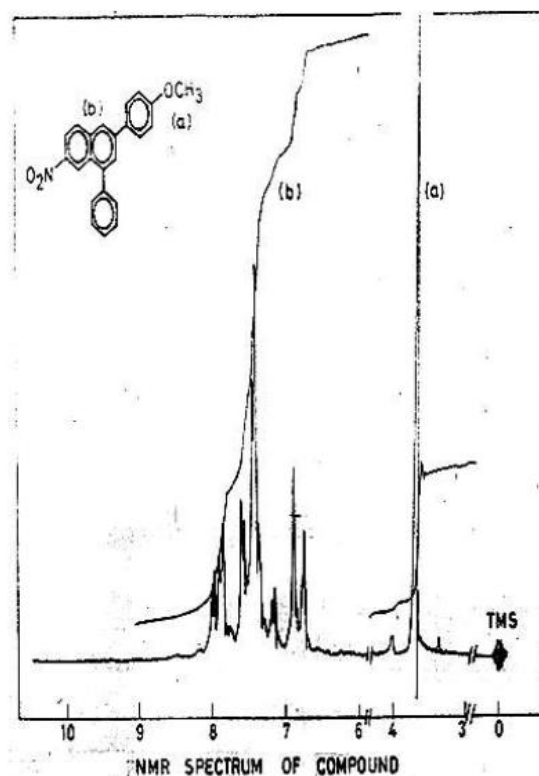
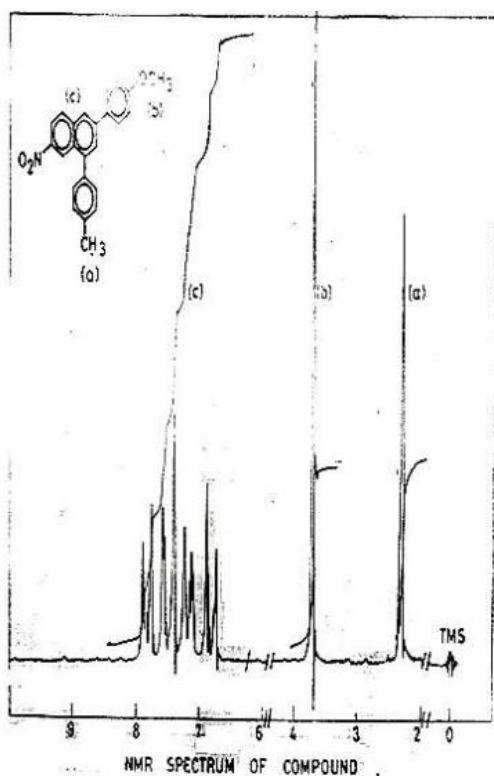


RESULT AND DISCUSSION:

Reaction of benzyl bromide and 4- nitro benzyl bromide with pyridine in benzene at reflux temperature gave benzyl pyridinium bromide and 4- nitrobenzyl pyridinium bromide. The structure of benzyl pyridinium bromide and 4- nitro benzyl pyridinium bromide were confirmed on the basis of NMR spectral data. The IR spectra of benzyl

pyridinium bromide and 4- nitro benzyl pyridinium bromide showed a diagnostic absorption band of strong intensity at 3045 and 3040 cm^{-1} respectively due to C-H stretching vibration band of methylene group attached to a position adjacent to nitrogen atom. Characteristic absorption bands due to NO_2 group in salt were obtained at 1515 and 1300 cm^{-1} . The NMR spectrum of salt showed singlet at 6.30 and 6.38 ppm due to the methylene protons and aromatic protons appeared in the range 6.80-9.35 ppm.





The reaction of these salt were carried out with a wide range of α , β - unsaturated carbonyl compounds in presence of anhydrous $AlCl_3$ or $ZnCl_2$ in mixture of sodium acetate and acetic acid at $200^\circ C$ to afford 1,3-diaxynaphthalenes and 1,3-diaxyl-7-nitronaphthalenes in 50-70% yields. It was however, observed that the yield of resulting naphthalene were dependent upon the nature of substituent's attached to pyridinium salt as well as to the, β - unsaturated ketones². The reactivity of salt 1, 3-diaxynaphthalenes and 1, 3-diaxyl-7-nitronaphthalenes because of -I effect of nitro group which stabilized the carbanion formation. Hence salt 1, 3-diaxyl-7-nitronaphthalenes affordable lower yield of naphthalene derivatives than salt 1, 3-diaxyl naphthalene²⁻⁴.

All naphthalene obtained in the present investigation was crystalline solids usually

soluble in chloroform, pyridine and acetone. All physical and spectral data have been given as the IR spectra of naphthalene derivatives showed a double absorption maximum in the region $1630-1620\text{ cm}^{-1}$ which were assigned to the stretching vibrations of C-C double bond. The strong bonds in region $900-850\text{ cm}^{-1}$ were diagnostic of polynuclear aromatics showed nitro group. The NMR spectra of compound, in general, exhibited aromatic multiple in the range $6.50-8.50$ ⁵.

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