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PRACTICAL SYNTHESIS OF PHEROMONE COMPONENTS OF ACHAEA JANATA (NOCTUIDAE)

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Abstract : A practical synthesis of pheromone components of Achaea janata utilising double alkylations on TosMIC as key steps has been achieved.

Castor culture has been one of the important crops of Indian subcontinent and active research to enhance the crop yields is most essential and desirable. Towards this goal, our group recently identified the Pheromone components of Achaea janata (Noctuidae)[1], which is the most noxious insect for castor crop especially when young crops are attacked. It is an oligophagus insect. Its main damage is defoliation by the larvae (castor), but in grapes loses caused by piercing of the fruits by the adults are more important. The chemicals isolated as pheromone blend included Heneicosane **(1)**, 6,9 (Z,Z) Heneicosadiene **(2)** and 3,6,9 (Z,Z,Z) Heneicosatriene **(3)**.

The isolation and identification of these chemicals has been so difficult that, about 200 female insects on careful extraction could produce hardly few nanograms of the sample. The availability of these chemicals in large quantities

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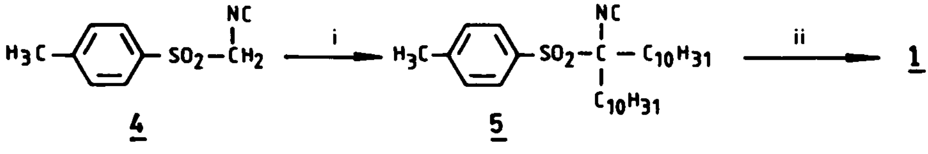
is essential for establishing bioefficacy and also for later application in the fields. Towards this end, herein we report our synthetic details for the synthesis of **1**,**2** and **3** following a common strategy.

In this connection we have utilized the TosMIC alkylation methodology for C-C bond formation using alkyl and alkenyl halides[2]. A convenient reduction of the alkylated TosMICs using Li/Liq NH_3, a methodology developed by our group[3], gave the corresponding pheromones in good yields.

Accordingly, TosMIC, **4** was dialkylated with 1-iododecane using NaH/ DMSO to give **5**, which on subsequent reduction with Li/Liq NH_3 gave pheromone **1**. **(Scheme 1)**

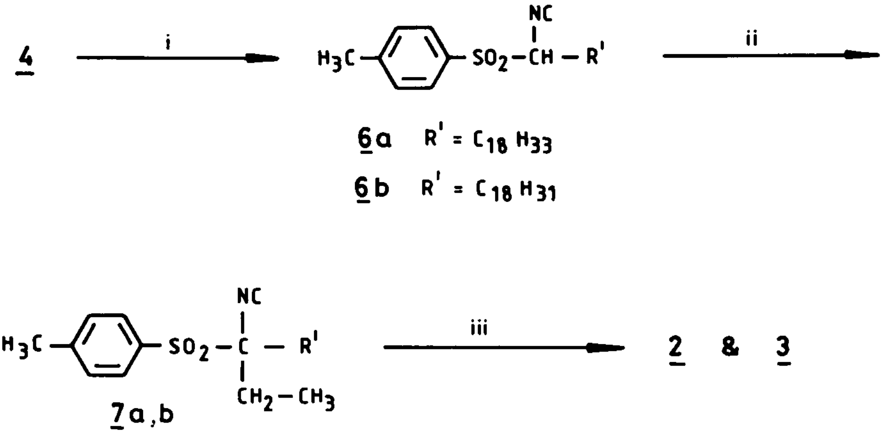
Scheme 1



Reagents :- i) NaH / DMSO/ether/ $C_{10}H_{31}I$
ii) Li / liq. NH_3

For the synthesis of diene and triene pheromones, Tosmic **4** was monoalkylated with the corresponding 6Z,9Z,18-iodo-octadecadiene and 3Z,6Z,9Z,18-iodo-octadecatriene[4] under NaOH/PTC conditions, to give **6a & 6b** respectively. Second alkylation with ethyl bromide under NaH/DMSO/ether conditions give their respective dialkylated products **7a and 7b**. These on reduction using Li/Liq NH_3 gave pheromones **2 and 3 (Scheme 2).**

Scheme 2



Reagents : i) 40% NaOH / DCM / $C_{18}H_{33}I$, $C_{18}H_{31}I$
ii) NaH / DMSO / ether / C_2H_5Br
iii) Li / liq. NH_3

We observed that the first alkylation of TosMIC using ethyl bromide always exclusively led to the dialkylated products. To over come this problem, the longer diene and triene iodides were mono alkylated followed by second alkylation with ethyl bromide. As the dialkylated products were found to be rather unstable, they are used without any further purification. During the TosMIC alkylation reactions, no traces of olefin isomerised products were observed. Thus an efficient and convenient method for the synthesis of pheromonal components of Achaea Janata has been developed starting from TosMIC.

EXPERIMENTAL

I.R spectra were recorded on perkin-elmer infrared 683 spectrophotometer. ^{1}H NMR spetra were recorded on varian gemini-200 MHz using TMS as an internal standard. Mass spectra were recorded on VG-70-70H double focussing mass spectrometer operating at 70 ev using direct inlet system.

Heneicosane 1 : To a suspension of prewashed sodium hydride (0.245g, 0.01 mol) in DMSO/ether (1:5, 18 ml) was added TosMIC **4** (1g, 0.005 mol) in ether (15 ml) at room temperature and after 10min, n-decyl iodide in ether was added drop wise and stirred at room temperature for 3h Reaction mixture was poured in water, organic layer was separated and aqueous layer was extracted with ether. The combined organic extracts were washed with water, brine, dried (Na_2SO_4), concentrated and afforded **5** (2.25g, 90%) as a gummy solid. It was used as such without further purification.

To liq NH_3 (50 ml) at -33°, was added Lithium (0.05g, 0.007mol), followed by dialkylated TosMIC **5** (0.342g, 0.0007mol) in ether (5ml) and ethanol (0.12ml). After 2h, ammonia was allowed to evaporate by bringing the reaction mixture to room temperature. Then water was added and extracted with ether. The organic layer was washed with water, brine, dried (Na_2SO_4), concentrated and on purification by column chromatography afforded pheromone **1** (0.182g, 90%) as white solid.

NMR : 0.9 (t, J = 6Hz, 6H, 2xCH_3), 1-1.6 (m, 38H, 19xCH_2)

Mass : m/z 296 (m^+)

M.P : 39-41° (lit : 40-41°)

Anal. calcd for $C_{21}H_{42}$: C, 85.63; H, 14.37. Found : C, 85.42; H, 14.26.

11-Tosyl Octadeca-6,9 (Z,Z) dienyl isocyanide,6a : A mixture of TosMIC **4** (2.92g, 0.015 mol), 6Z,9Z,18 - Iodo - octadecadiene (5.74g, 0.015 mol),tetrabutyl ammonium bromide (0.960g,0.003 mol),40% aqueous NaOH (45 ml) and DCM (45 ml) was stirred at 0° for 2h and then at room temperature for 12h. The reaction mixture was diluted with water and extracted with dichloromethane. The organic layer was washed with water, brine, dried (Na_2SO_4), concentrated and on purification by column chromatography gave **6**. (5.316g, 80%) as a gummy solid.

NMR -: 0.8 (dt, 3H, CH_3), 1.2-1.5(m, 4H, 2XCH_2), 2.5(s, 3H, Ar-CH_3), 2.7(m, 2H), 4.4(m,1H,CHNC), 5.3(m, 4H, Olefinic), 7.20(d, J=8Hz, 2H Ar-H), 7.60(d, J=8Hz, 2H, Ar-H)

I.R (neat) : ν_{max} 3010,2965,2875,2120,1650,1350,1170 cm^{-1}

Anal. Calcd. for $C_{27}H_{41}NO_2S$: C, 73.09; H, 9.31. Found : C, 73.08; H, 9.31.

6,9 (Z,Z) Heneicosadiene 2 : Compound **7a** was prepared by using ethyl bromide (0.218g, 0.002 mol) and monoalkylated TosMIC **6a** (1g, 0.002 mol) by adopting the same procedure as described for **5** to afford **7a** (0.471g, 50%). It was used as such without much purification.

The dialkylated TosMIC **7a** was reduced by adopting the above procedure as described for **1** using dialkylated TosMIC **7a** (0.32g, 0.0007 mol), lithum (50mg, 0.007 mol) to obtain pheromone **2** (0.163g,80%) as colourless oil.

NMR : 0.89 (t, J = 6Hz, 6H, 2xCH_3), 1.15 - 1.45 (m, 24H, 12xCH_2), 1.95 - 2.1 (m, 4H, allylic methylenes), 2.6 - 2.8 (m,2H, skipped methylene), 5.3 (m,4H, olefinic).

I.R (neat) : ν_{max} 3008,2956,2914,2852,1468 cm^{-1}

Mass : m/z 292 (m^+), 67 (100).

Anal. Calcd. for $C_{21}H_{40}$: C, 86.21; H, 13.78. Found : C, 86.20; H, 13.75.

19-Tosyl-19-3,6,9,(Z,Z,Z) Heneicosatrienyl Isocyanide 6b : Compound **8** was prepared using 3Z,6Z,9Z - iodo - octadecatriene (5.61g, 0.015 mol) TosMIC **4** (2.92g, 0.015 mol) by describing the same procedure as described for **1** to obtain **6b** (4.63 g, 70%) as a gummy solid.

NMR : 0.9 (dt, 3H, CH_3), 1.2(bs, 14H, $7XCH_2$), 2 (m, 4H, $2XCH_2$), 2.5(s, 3H, Ar-CH_3), 2.7 (m, 4H, $2XCH_2$), 4.4 (m,1H, CHNC), 5.3(m, 6H, Olefin), 7.20(d, J=8 Hz, 2H, Ar-H), 7.60(d, J=8 Hz, 2H, Ar-H).

I.R (neat) : ν_{max} 3010,2965,2870,2120,1350,1170 cm^{-1} .

Anal. Calcd for $C_{27}H_{39}NO_2S$: C, 73.42; H, 8.89. Found : C, 73.30; H, 8.75.

3,6,9 (Z,Z,Z) Heneicosatriene 3 : Compound **7b** was prepared using ethyl bromide (0.218g, 0.002 mol),monoalkylated TosMIC **6b** (1g, 0.002 mol) and NaH (0.096 g, 0.002 mol) by adapting the same procedure as described for **5** to yield **7b** (0.48 g, 52%). The dialkylated TosMIC **6b** was reduced by adopting the same procedure as described for **1** using dialkylated TosMIC **6b** (0.328 g. 0.007 mol) and lithium (50 mg, 0.007 mol) to obtain pheromone **3** (0.15g, 75%) as colourless oil.

NMR : 0.85-1.5 (m, 6H, $2xCH_3$), 1.2 - 1.4 (bs, 18H, $9xCH_2$), 1.95 -2.15 (m, 4H, allylic methylenes), 2.65 -2.85 (m, 4H, skipped methylenes), 5.35 (m,6H,olefinic)

I.R (neat) : ν_{max} 3010,2956,2914,2852,1452,1468 cm^{-1}

Mass : m/z 290 (m^+), 67 (100).

Anal. Calcd. for $C_{21}H_{38}$: C, 86.81; H, 13.18. Found : C, 86.70; H, 13.08.

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6. IICT communication # 3956.

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