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# CONFIGURATIONAL ASSIGNMENT OF COMPOUNDS (DIELS-ALDER DERIVATIVES) THROUGH $^1$H NMR SPECTROSCOPY

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## ABSTRACT

**Role of $^1$H NMR spectroscopy is explored in configurational assignment of derivatives of Diels-Alder adducts through conformational analysis of $N_{sp}{}^2C_{sp}{}^3$ bond. The proposed geometry of compounds is quite satisfactory on steric grounds.**

**KEYWORDS:** Configuration; Conformation; NMR Spectroscopy

Many physical methods have been successfully used for configurational assignment. The NMR spectroscopy surpassed all other techniques. The advantage of this technique lies in its versatile applicability and in the ease of obtaining spectra and spectral interpretation in exploring the minute details of molecular structure (Srivastav *et al.*, 1993) (Srivastav *et al.*, 1999) (Srivastav, 2015) (Srivastav *et al.*, 1994).

In this paper, using conformational analysis through $^1$H NMR spectroscopy and configurational assignment is determined.

Succinimidyl derivatives have shown a fast rotation about $N_{sp}{}^2$ -$C_{sp}{}^3$ bond at the NMR time scale. An attempt to restrict rotation about $N_{sp}{}^2$-$C_{sp}{}^3$ bond has been made by substituting a bromine atom at the benzyl carbon, bromo derivatives (ii) and (iv) have been prepared (Verma and Singh, 1977) (Djerassi, 1948) (Hoi and Rend, 1946).

## EXPERIMENTAL PROCEDURE

General melting point were determined on Buch melting point apparatus and are uncorrected. The analytical data of C, H and N were determined in Perkin-Elmer C, H and N Analyzer (Model no. 240C), IR spectra were recorded in KBr on JASCO-FT/IR-5300 Spectrometer. $^1$H NMR spectra were recorded on a ZELO FX 90Q multinuclear spectrometer in CDCI3.

1. Compound (i), (iii) and (v) were obtained by heating the adduct with equimolar amount of the corresponding amines in round bottom flask at 120-30o on an oil bath for about 3-4 hours, products were recrystallized from benzene.

Preparation of compounds (Bromination of the benzylic hydrogen) Compound (ii) and (iv) dissolved in benzene and was treated with equimolar amount of bromine (in carbon tetrachloride), the mixer was exposed to light at room temperature. Bromo derivative (ii) separated after six hours as pasty powder. It was recrystallized from n-hexane.

Bromination of furfuryl hydrogen by N-Bromo succinimide (NBS).

2. Compound (iv) was prepared according to method of Whol-Ziegler[6] Compound (iii) (3.5g) dissolved in carbon tetrachloride(30ml) and (1.8g) NBS was added. The mixture was refluxed for two hours and product was recrystallized from benzene.

## RESULTS AND DISCUSSION

The spectrum of compound (ii) exhibit a singlet at δ 4.22(1H) for the -CHBrPh proton along with other normal resonances and it is similar to the spectrum of N-benzyl derivative (i). The replacement of one of the hydrogens with a bromine atom would deshield the methyne proton resonance (about 1.5 ppm) and its appearance at the normal position suggests a preferred conformation, where the methyne proton lies in the shielding zone of the cage phenyl ring (1). Restricted rotation about $N_{sp}{}^2$-$C_{sp}{}^3$ bond and a preferred conformation with the methine proton in syn orientation with in syn orientation is consistence with the observation shielding parameters. The resonance of α, β – protons have been quite diagnostic in the determination of the geometry of the substituents (Br and $C_6H_5$) are out of the plane to influence the magnetic environment of α and β – protons.

The proposed geometry is quite satisfactory on the steric ground. Compounds (iv) obtained by the bromination of N-furfuryl derivative (iii) with N-bromo

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succinimide exhibit a singlet at δ 4.20 (1H) for the -CHBr and other resonances (Table 1) on the consideration of shielding parameter of a methine proton, a preferred geometry about N-C bond having the hydrogen syn-orientation similar to compound (ii) is proposed (2).

Compound (v) forms Diels -Alder adduct with N-Ortho-tolylmaleimide. The methylene protons appear as an AB quartet centered at δ 3.0 (Table 1). The magnetic non-equivalence of methylene protons may result from the chiral furfuryl moiety. The appearance of methylene protons at a shielded position (Δδ=1.2 ppm) suggests a preferred conformation (3) where the methylene protons are in synorientation.

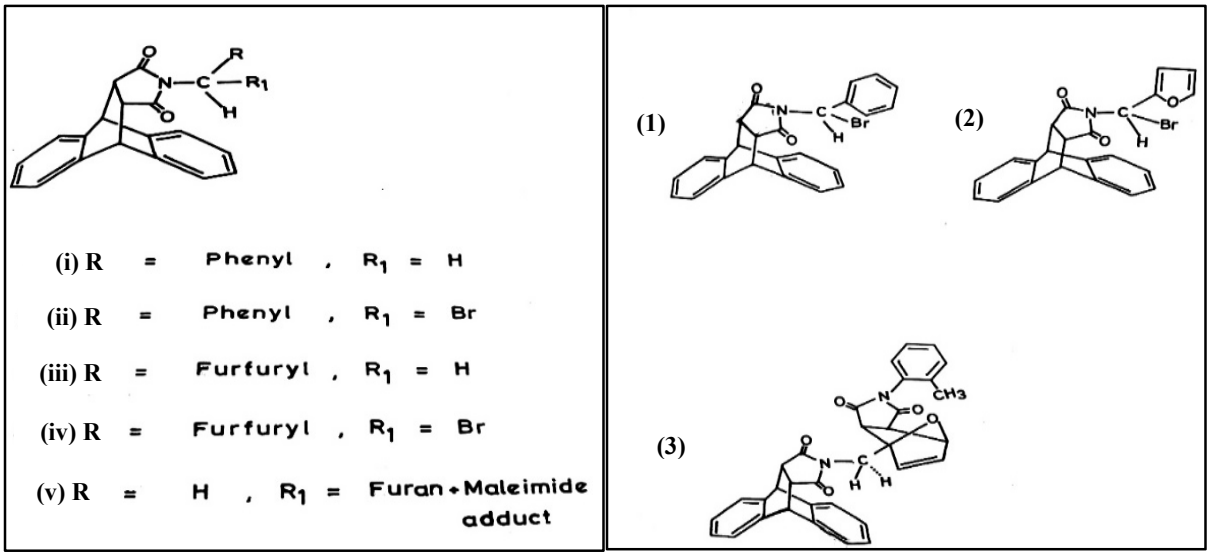


**Figure 1: (a) preparation of compounds from (i) to (v); (b) configurational assignment of the compound (i), (ii) & (iii)**

**Table 1: $^1$H NMR Data of Compounds (i to v)**

| | |
|---|---|
| (i) | δ3.35(bs,2H,α-,β -H),δ4.20(S,2H, benzylic – CH2 protons).δ4.90(bs,2H,9- and 10-H), δ6.8-7.3 (bm,13H,aromatic protons) |
| (ii) | δ3.38(bs,2H,α-,β -H),δ4.22(S,1H,-CHBrPh).δ4.92(bs,2H,9- and 10-H), δ7.0-7.5 (bm,13H,aromatic protons) |
| (iii) | δ3.2(bs,2H,α-,β -H),δ4.19(S,2H,furfuryl – CH2 protons).δ4.80(bs,2H,9- and 10-H), δ5.68(m1H,4'1-H), δ6.10(m,1H,3'1-H),δ5.8 -7.35(bm,9H aromatic and 5'1-H protons) |
| (iv) | δ3.3(bs,2H,α-,β -H),δ4.20(S,1H,-CHBr- protons).δ4.80(bs,2H,9- and 10-H), δ5.70(m1H,4'1-H), δ6.10(m,1H,3'1-H),δ6.8 -7.4(bm,9H aromatic and 5'1-H protons) |
| (v) | δ3.0(AB Qurtet,2H,CH2-furfuryl protons)δ3.3(bs,2H,α-,β -H),δ4.9(S,2H,9- and 10- H),resonances of furfuryl moiety:δ2.5(s,3H,2'-CH3), δ3.9 (m,2H,2-and 3-H),δ5.1(s,1H,1'-H),δ6.5(d,2H,olefinic protons),δ7.0-7.5(bm,12H,aromatic protons) |

**Table 2: Identification of Prepared Compounds**

| Chemical formula of compounds | Melting Point ($^0$C) | I. R data of compounds |
|---|---|---|
| C25H19O2N | 235-37 | 1780m,1710s,1610w |
| C25H18O2NBr | 187-89 | 1778m,1720s,1600w |
| C23H17O3N | 220-22 | 1780w,1720s,1600w |
| C23H16O3NBr | 201-03 | 1790m,1710s,1620w |
| C37H26O5N2 | 228-29 | 1780m,1710s,1610w |

## CONCLUSION

Configurational assignment of compounds (ii, iv & v) are determined with help of conformational analysis through $^{1}$HNMR spectroscopy successfully.

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## REFERENCES

Djerassi C., 1948. Chem, *Rev*., **43**: 271.

Hoi B. and Rend L., 1946. J. Compt., **222**: 1441.

Srivastav Kamal K., Verma Ashok K. and Verma Shiva M.,1993. Indian Journal of Chemistry, **32**B: 1143.

Srivastav Kamal K., Srivastav V. and Verma Shiva M., 1999. Indian Journal of Chemistry, **38**B: 672.

Srivastava Kamal K., 2015. Journal of Chemistry in Asia, **6**: 4-5.

Srivastava A., Srivastava V. and Verma Shiva M., 1994. J. Org. Chem., **59**: 3460-3563.

Verma S.M. and Singh M.D., 1977. J. Org. Chem., **42**: 3736.