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Synthesis, characterization and study of potential reactions of tertiary amino aldehydes

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ABSTRACT

p-NN-diethylamino benzaldehyde has set a series of reactions with substituted glycines, rhodanine, hydantoin, thiohydantoin, malon anilic acids and substituted malon anilic acid hydrazides, fluorene and cyanoacetamide. The product obtained in each condensation has been isolated, purified and identified by elemental analysis. The study of the position of formyl group in the benzene ring and its reactive nature (I, II and III) has been done on the basis of IR, NMR spectral data of the aldehyde (I). The study reveals that on the theoretical bases the substitution of formyl group will be in the meta position with respect to the cyanoethyl group of the benzene ring. So it is possible that the aldehyde (I) may have been the proposed structure and same for the other aldehydes (II & III).

Key words: p-NN-diethylaminobenzaldehyde, characterization, tertiary amino benzaldehyde, series of condensation reactions.

INTRODUCTION

Tertiary amino benzaldehydes have been found considerable use in synthetic organic chemistry. Their importance is strikingly evident from their role in the synthesis of dyes, chemotherapeutic agents, analytical reagents and a variety of other compounds. The procedure described by Campaigne and Archer[1] offers a convenient and general method for the synthesis of aromatic tertiary amino aldehydes. We have adopted the same procedure for the synthesis of p-NN-diethylamino benzaldehyde. A series of condensation reactions of the aldehyde was taken up, because of the various practical applications of the products obtained. Some of these are briefly discussed. Rhodanine derivative has been found to be a good reagent for detecting, copper, silver and mercury. In the observations deep red colour with silver and mercury and brownish red colour with cuprous ions were obtained.

Holan et al[2] have reported marked hypoglycaemic activity of thiohydantoin and hydantoin derivatives. The active moiety in hydantoin and thiohydantoin have been found to lower the blood sugar level in mammals. Therefore hydantoin and thiohydantoin derivatives are prepared.

Schiff bases have been recently used for the formation of complexes of tetravalent[3] cobalt. We have synthesized a new set to Schiff Bases by the condensation of tertiary amino aldehydes with a variety of primary aromatic amines.

Acid hydrazones have been found to possess antibacterial properties.[4,5] In addition they have also been reported to possess antifungal[6,] as well as insecticidal activity.[7] The hydrazones were found to inhibit partially or completely the growth of *S. aureus, E. coli* and *B. subtilis*.

Fluorene derivatives have gained importance as plant hormones, wetting agents and as dyes.[8] Thus a new fluorene derivative has been synthesised.

Oxazolones are found useful as reagents for the naturally occuring acyl glycines by paper

chromatograp.[9] Therefore a new series of oxazolones have been prepared.

MATERIAL AND METHODS

All the melting points reported in this paper were determined by the open capillary using melting point apparatus and are uncorrected. The purity of all the products were determined by thin layer chromatography. The IR, NMR spectra of the aldehyde for structure establishment has been done at CDRI Lucknow.

The analytical data, colour, melting points & yield % of the prepared compounds is recorded in Table I.

EXPERIMENTAL

The series of established reactions is shown in Fig. I.

Procedure for preparation of Rhodanine derivative (Compd No. 7-8)

A mixture of aldehyde (0.01 mole), rhodanine (0.01 mole) and glacial acetic acid (5 ml) is refluxed for 2 hours. On cooling brick red shining crystals were obtained. Recrystallised from acetone.

Procedure for preparation of thiohydantoin derivative (Compd No. 12)

Prepared by heating aldehyde (0.01 mole), thiohydontoin (0.01 mole), fused sodium acetate (0.1) and acetic anhydride (0.5 ml) for 4 hours at 150-155°C. On cooling chocolate coloured crystals were obtained. Recrystallised by further washings with boiling ethanol, methanol and acetone.

Procedure for preparation of hydontoin derivative (Compd. No. 11)

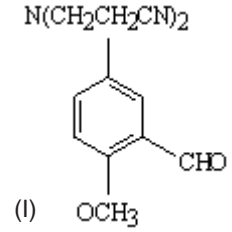
A mixture of aldehyde (0.01 mole), hydantoin (0.01 mole), glacial acetic acid and dry benzene (10 ml) was heated for 3 hours in a 25 ml r.b. flask attached to a constant water separator (Dean and Start's apparatus). Solid obtained is recrystallised from ethanol.

Procedure for preparation of Schiff Bases (Compd. No. 9-10)

A mixture of aldehyde (0.01 mole) and amine (0.01 mole), absolute ethanol (5 ml) and 2 drops of piperidine were refluxed for 2 hours. It was cooled and left over night. The pale yellow crystals were obtained and recrystallised from ethanol.

Procedure for preparation of Acid Hydrazones (Compd. No. 13-22)

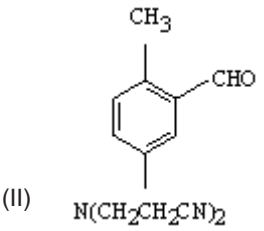
A mixture of aldehyde (0.01 mole) and acid hydrazide (0.01 mole) in ethanol (10 ml) was refluxed for 2 hours. The white crystals obtained were recrystallised from ethanol.



(I)

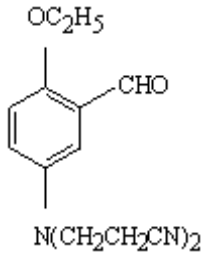
2methoxy-5-NN-bis-2'-cyanoethylamino benzaldehyde

On the above basis the structure of other aldehydes was also established



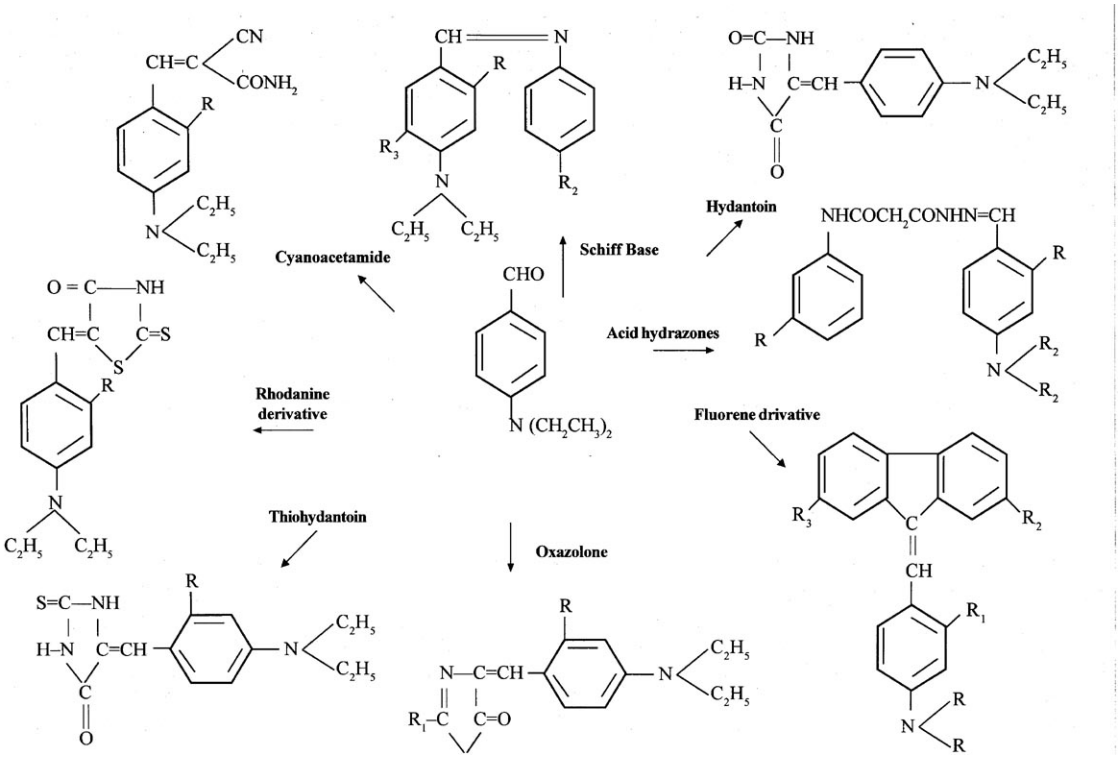
(II)

2-methyl-5-NN-bis-2'-cyanoethylamino benzaldehyde



(III)

2-ethoxy-5-NN-bis-2'-cyanoethylamino benzaldehyde



Scheme

Procedure for preparation of Cyanoacetamide (Compd. No. 24)

A mixture of aldehyde (0.01 mole) cyanoacetamide (0.01 mole), absolute ethanol (10 ml) and 2 drops of pyridine. Yellow crystals obtained were recrystallised from ethanol.

Procedure for preparation of fluorene derivative (Compd. No. 23)

A mixture of aldehyde (0.01 mole), 2,7-dinitrofluorene (0.01 mole) and piperidine (4 drops) and dry benzene (15 ml) over a steam bath for 4 hours. Solid obtained was recrystallised by washing with boiling glacial acetic acid and ethanol.

Procedure for preparation of Oxazolones (Compd. No. 1-6)

A mixture of aldehyde (0.01 mole), hippuric acid (0.01 mole) and fused sodium acetate (0.08 gm) and acetic anhydride (0.5 ml) were mixed and heated at 100°C for 2 hours. On cooling bright orange needles were obtained Recrystallised from acetone.

RESULTS AND DISCUSSION

An attempt has been made to establish the structure of the aldehyde obtained after formylation. The IR and NMR spectra[10-12] of the compound (I) was analysed. The IR spectrum reveals peaks at 1600 cm^{-1}, 1580 cm^{-1} and 1450 cm^{-1} for aromatic character. A strong absorption peak at 1680 cm^{-1} confirms the presence of aromatic aldehydic gp. A strong band at 1380 cm^{-1} and 1280 cm^{-1} shows aromatic tertiary amine.

Absorption at 2250 cm^{-1} and 1040 cm^{-1} can be attributed to cyanine and methoxy gps. The absorption at 2900 cm^{-1} can be taken for CH_2 gp. Moreover absorption at 700 cm^{-1}, 890 cm^{-1} and 850 cm^{-1} are good support for the possibility of 1:3:4 type of substitution on benzene ring.

Table 1: Physical data and elemental analysis of the compounds derived from p-NN-diethyl amino benzaldehyde

S. No.	Compound Name	Colour	Mpt.	Yield	Nitrogen%found (calculated)
1.	2-Phenyl-4-(p-NN-diethylamino benzylidene)-5-oxazolone	Red	131	68.31	9.15 (8.75)
2.	2-(m-nitrophenyl)-4-(p-NN-diethylamino benzylidene)-5-oxazolone)	Red	207	73.65	12.18 (11.50)
3.	2-(3:5[1]-dinitrrophenyl) -4-(p-NN-diethylamino benzylidene)-5-oxazolone)	Red	234	72.06	12.92 (13.65)
4.	2(o-chlorophenyl) -4-(p-NN-diethylamino benzylidene)-5-oxazolone)	Orange	116	75.0	7.87 (7.89)
5.	2-(p-methoxyphenyl) -4-(p-NN-diethylamino benzylidene)-5-oxazolone)	Red	181	83.32	8.26 (8.00)
6.	2-Styryl-4-(p-NN-diethylamino benzylidene)-5-oxazolone)	Red	138	63.34	8.29 (8.09)
7.	p-NN-2diethlamino benzylidene rhodonine	Red	208	77.57	9.88 (9.59)
8.	4-NN-2'-diethylamino-1-naphthalidene rhodanine	Purple	215	76.66	8.69 (8.18)
9.	p-NN-diethylamino benzylidene-β-naphthylamine	Yellow	157	74.32	15.16 (14.65)
10.	p-NN-diethylamino benzylidene-p-aminodiphenyl	Pale Yellow	185	78.05	14.43 (14.14)
11.	p-diethylamino benzylidene hydantoin	Yellow	250	75.61	16.71 (16.21)
12.	p-Diethylamino benzylidene thiohydontoin	Chocolate	268	77.74	15.17 (15.27)
13.	Malon-anilic acid hydrazone	White	195	88.42	15.49 (15.90)
14.	Malon-o-toluidic acid hydrazone	White	174	65.81	15.14 (15.30)
15.	Malon-m-toluidic acid hydrazone	White	170	65.85	15.10 (15.30)
16.	Malon-o-chloroanilic acid hydrazone	White	160	68.12	13.81 (14.48)
17.	Malon-p-chloroanilic acid hydrazone	White	217	78.14	13.87 (14.48)
18.	Malon-2:6-xylidic acid hydrazone	White	202	75.78	14.04 (14.74)
19.	Malon-5-chloro-o-toluidic acid hydrazone	White	182	95	13.20 (13.97)
20.	Malon-p-anisidic acid hydrazone	White	179	87.70	14.42 (14.65)
21.	Malon-p-phenetidic acid hydrazone	White	189	70	13.62 (14.14)
22.	N-β-naphthyl-malon-amic acid hydrazone	White	200	72	13.89 (13.93)
23.	2:7 dinitro-9-(p-diethylamino benzylidene) fluorene	Red	209	85.71	10.30 (10.12)

The NMR spectrum confirms the assigned structure and shows signals due to methylene protons and 2 triplets centered around 4.38 τ and 7.40 τ. Signal at 4.38 τ is assigned to deshielded methylene protons in the vicinity of CN gp and signals at 7.40 τ is assigned to methylene proton attached to nitrogen. Aromatic protons appear as a multiplet centered around 2.50 τ.

By this spectral study it was reasonable to think on a theoretical basis that under acidic conditions, the tertiary amino gp will be protonated and thus bring about a meta orientation while the methoxyl gp will favour ortho substitution as para is already occupied. Thus the possible structure of this aldehyde may be:

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