

A Study on the Preparation and Reactions of 2-methyl-4-dimethylaminobenzaldehyde

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2-Methyl-4-NN-dimethylaminobenzaldehyde was prepared by formylating 2-methyl-4-NN-dimethylaniline using dimethyl formamide and its identity established by the preparation of its oxime, 2:4 DNP, semiacarbazone, azine etc. and also by studying its I. R. spectrum. The aldehyde has been condensed with cyanacetamide, ethylcyanacetate, malono-nitrile, rhodanine, nitromethane, hydantoin, thio-hydantoin, iso-nicotinic acid hydrazide and the products isolated and identified. The aldehyde has also been condensed with benzoyl, cinnamoyl, anisoyl, *o*- and *p*-chlorobenzoyl and *m*- and *p*-nitrobenzoyl glycines and the corresponding 5(4) oxazolones obtained.

Preliminary experiments show that the aldehyde can be used as a reagent for the chromatographic detection of acyl glycines and the rhodanine derivative as a reagent for detection of certain metals.

Several methods are known for the formylation of the aromatic nucleus.¹ Duff and Bills² formylated phenols using hexamine and later Duff³ extended the method to the formylation of NN-dialkylanilines. N-Methyl formanilide and dimethyl formamide (DMF) are very good reagents for introducing the formyl group in an aromatic nucleus. Campaigne and Archer⁴ found DMF superior to N-methyl formanilide for the formylation of NN-diethyl aniline. Observations made in this laboratory also confirm the view.^{5,6} Duff³ has prepared 2-methyl-4-NN-dimethylaminobenzaldehyde using hexamine. Now the same aldehyde has been prepared using DMF and yield obtained is better. The identity of the aldehyde has been established by preparing its 2:4 dinitrophenyl hydrazone, phenyl hydrazone, semicarbazone and oxime. Further, the I. R. spectrum shows the Ar-CHO band at 1675 cm^{-1} and the Ar-N(CH₃)₂ band at 2775 cm^{-1} .

This aldehyde has now been condensed with hydrazine, iso-nicotinic hydrazide, cyanacetamide, ethyl cyanacetate, malono-nitrile, nitro-methane, rhodanine, hydantoin and thio-hydantoin and the products identified not only by chemical methods but also by studying their I. R. spectra. A number of 5(4) oxazolones have also been prepared by condensing the aldehyde with acyl glycines. The oxazolones vary from orange to deep red in colour and from 30 to 70% and yield. The analytical results, m.p. etc. are given in Table No. I.

Some of the possible practical applications of the condensation products are being investigated. The rhodanine derivative gives reddish violet colour with silver salts, brown colour with cuprous salts and light brown colour with mercurous salts. This

1. Lloyd N. Ferguson, *Chem. Rev.*, 1946, **38**, 227.
2. J. C. Duff and E. J. Bills, *J. Chem. Soc.*, 1932, 1987; 1934, 1305.
3. J. C. Duff, *J. Chem. Soc.*, 1945, 276.
4. E. Campaigne and Wesley L. Archer, *J. Amer. Chem. Soc.*, 1953, **75**, 989.
5. Abraham Thomas and P. I. Ittyerah, *Jour. Indian Chem. Soc.*, 1964, **41**, 38.
6. O. P. Singhal, (Km.) Veena Gupta and P. I. Ittyerah, *Indian J. Appl. Chem.*, 1966, **29**, 69.

observation suggests that the rhodanine derivative of the aldehyde can be used for the qualitative detection of copper, silver and mercury salts by a simple spot test technique on filter paper strips. Further, the deeply coloured 5(4) oxazolones obtained by the condensation of 2-methyl-4-*NN*-dimethylaminobenzaldehyde with acyl glycines also suggests that the aldehyde can be used as a reagent in the detection of naturally occurring acyl glycines. The method adopted for the preparation of oxazolones, is the same as that recommended by Acheson and others⁷ in the case of dimethylaminobenzaldehyde and dimethylamino cinnamaldehyde.

TABLE I

Name	Formula	m.p. °C.	Yield %	% Nitrogen	
				Found	Calculated.
2-Phenyl-4-R	C ₁₉ H ₁₈ N ₂ O ₂	192	41.7	9.4	9.2
2-Styryl-4-R	C ₂₁ H ₂₀ N ₂ O ₂	172	31.5	8.05	8.43
2-(<i>p</i> -Methoxy phenyl)-4-R	C ₂₀ H ₂₀ N ₂ O ₃	242	67	8.12	8.33
2-(<i>o</i> -Chlorophenyl)-4-R	C ₁₉ H ₁₇ N ₂ O ₂ Cl	176	35.3	8.37	8.22
2-(<i>p</i> -Chlorophenyl)-4-R	C ₁₉ H ₁₇ N ₂ O ₂ Cl	229	44.1	8.53	8.22
2-(<i>m</i> -Nitrophenyl)-4-R	C ₁₉ H ₁₇ N ₃ O ₄	222	51.7	11.71	11.96
2-(<i>p</i> -Nitrophenyl)-4-R	C ₁₈ H ₁₇ N ₃ O ₄	282	58.3	11.69	11.96

Where R stands for (2'-methyl-4'-*NN*-dimethylaminobenzylidene)-5-oxazolone.

Because of the practical uses mentioned above it was considered worthwhile to prepare 2-methyl-4-*NN*-dimethylaminobenzaldehyde and study some of its important reactions.

EXPERIMENTAL

Formylation of NN-dimethyl-m-toluidine using dimethylformamide; formation of 2-methyl-4-NN-dimethylaminobenzaldehyde. *NN*-Dimethyl *m*-toluidine (16 g., 0.34 mol.), phosphorous oxychloride (18 g., 0.34 mol.) and dimethyl formamide (30 g., 1.2 mol.) were taken in a round bottomed flask fitted with a mechanical stirrer and a reflux condenser. The contents became hot during mixing the reactants and so the flask was cooled. After mixing it was heated on a steam bath for 3 hr. with stirring. The dark brown viscous product obtained was poured over crushed ice. To the homogeneous solution obtained was added crystalline sodium acetate till there was a distinct smell of acetic acid. On keeping overnight the aldehyde separated as a crystalline solid with a pale violet tint. The crude product was purified by recrystallisation from aqueous ethanol forming white shining needles. It melted at 70°, yield, 8 g. (41.4%), (lit³, m.p. 67° and yield 19%) Found: N, 8.7%; Calc. for C₁₀H₁₃NO: N, 8.6%.

The 2,4-*DNP* of the aldehyde was obtained as deep red crystals, insoluble in most of the organic solvents. It was purified by washing with hot ethanol, m.p. 252°. Found: N, 20.18%, Calc. for C₁₆H₁₇N₅O₄: N, 20.41%.

The *phenylhydrazone* of the aldehyde was prepared in the usual manner and after recrystallisation from methanol it melted at 150°, Found: N, 16.52%, Calc. for C₁₆H₁₉N₃: N, 16.6%.

The *semicarbazone* of the aldehyde was obtained as a white crystalline solid. After purification from ethanol, it melted at 238°. Found: N, 25.48%; Calc. for $C_{11}H_{16}N_4O$: N, 25.45%.

The *oxime* of the aldehyde obtained was purified by repeated recrystallisation from aqueous ethanol and melted at 112°.

Found: N, 15.90%; Calc. for $C_{10}H_{14}N_2O$: N, 15.73%.

The *azine* of the aldehyde was prepared by refluxing a mixture of the aldehyde (0.5 g.), hydrazine hydrate (0.2 g.), glacial acetic acid (5 ml.) and ethanol (10 ml.) for half an hour. The yellow crystalline product obtained was purified by recrystallisation from a large volume of acetone. It melted at 220°, yield 0.35 g. (35.8%).

Found: N, 17.48%. Calc. for $C_{20}H_{26}N_4$: N, 17.40%.

2-Methyl-4-NN-dimethylaminobenzylidene cyanacetamide—was prepared by heating a mixture of the aldehyde (0.8 g.), and cyanacetamide (0.42 g.) with two drops of piperidine in an oil bath at 100°-105° for 3 hr. The yellow solid obtained was purified by recrystallisation from ethanol forming shining yellow needles, m.p. 221°, yield 0.8 g. (72.8%).

Found N, 18.21%; Calc. for $C_{13}H_{15}N_3O$: N, 18.34%.

2-Methyl-4-NN-dimethylaminobenzylidene cyanacetate was obtained as an orange red solid, on heating equimolecular amounts of the aldehyde (0.8 g.) and ethyl-cyanacetate (0.56 g.) with two drops of piperidine, in an oil bath at 100-105° for 4 hr. It was purified by recrystallisation from aqueous ethanol and melted at 117°, yield 1.0 g. (80.6%).

Found N, 10.80%. Calc. for $C_{15}H_{18}N_2O_2$: N, 10.85%.

2-Methyl-4-NN-dimethylaminobenzylidene malononitrile was prepared by refluxing a mixture of aldehyde (0.54 g.), malono-nitrile (0.22 g.), dry crystals of ammonium acetate (0.2 g.), glacial acetic acid (1 ml.) and dry benzene (15. ml.) for 4 hr. in a flask fitted with a Dean-Stark constant water separator. The yellow needles obtained on cooling, were collected and recrystallised from acetone, m.p. 207°, yield, 0.52 g. (74.3%).

Found: N, 20.05%. Calc. for $C_{13}H_{13}N_3$: N, 19.9%.

2-Methyl-4-NN-dimethylaminobenzylidene rhodanine was obtained as a brick red solid, by gently refluxing a mixture of the aldehyde (0.8 g.), rhodanine (0.66 g.) and glacial acetic acid (10 ml.) for 4 hr. It was purified by recrystallisation from a large volume of acetone forming dark red shining plates, m.p. 279°; yield 0.35 g. (25.0%).

Found: N, 10.12%; S, 23.11%. Calc. for $C_{13}H_{11}N_2S_2O_2$: N, 10.97%; S, 23.02%.

2-Methyl-4-NN-dimethylamino-B-nitro-styrene. A mixture of the aldehyde (1 g.), nitromethane (1 ml.), ammonium acetate (0.4 g.) and glacial acetic acid (5. ml.) were heated in an oil bath maintained at 105°-110° for 4 hr. The yellow crystalline solid obtained was collected and recrystallised from glacial acetic acid melted at 145°, yield, 0.92 g. (76.6%). Found: N, 14.72%. Calc. for $C_{10}H_{12}N_2O_2$: N, 14.58%.

Iso-nicotinic acid hydrazone of 2-methyl-4-NN-dimethylaminobenzaldehyde was obtained as a pale yellow crystalline product by refluxing a mixture of the aldehyde (0.42 g.), isonicotinic hydrazide (0.32 g.) and aqueous ethanol (20 ml., 50%) for 2 hr.

It was purified by using dilute ethanol. m.p., 202°, yield, 0.52 g. (74.3%). Found: N, 19.72%; Calc. for $C_{16}H_{18}N_4O$: N, 19.86%.

2-Methyl-4-NN-dimethylaminobenzylidene hydantoin was prepared by gently refluxing a mixture of the aldehyde (0.84 g.), hydantoin (0.5 g.), fused sodium acetate (0.5 g.), glacial acetic acid (2.5 ml.) and two drops of acetic anhydride in an oil bath (140°-45°) for 5 hr. The crude product was repeatedly washed with absolute alcohol. It melted at 221°, yield, 1.1g. (91.7%). Found: N, 18.38%. Calc. for $C_{12}H_{15}N_3O_2$: N, 18.02%.

2-Methyl-4-NN-dimethylaminobenzylidene thio-hydantoin was prepared in the same manner as the hydantoin derivative. The temperature of the oil bath was maintained at 120°-125°. The crude product was purified by recrystallisation from methyl alcohol. m.p. 242°, yield (56%).

Found : N, 16.43%; S, 12.678%. Calc. for $C_{12}H_{15}N_3SO$: N, 16.86%; S, 12.851%.

2-phenyl-4-(2'-methyl-4'-NN-dimethylaminobenzylidene) -5-oxazolone : The synthesis of this compound as a representative of the 5(4)-oxazolones, derived from 2-methyl-4-NN-dimethylaminobenzaldehyde is described below :

Hippuric acid (0.85 g.), 2-methyl-4-NN-dimethylaminobenzaldehyde (0.8 g.), fused sodium acetate (0.42 g.) and acetic anhydride (3 ml.) were mixed and heated on a steam bath for 2 hr. A clear brown solution was first obtained but within 10 mins, a dark red solid started separating. It was collected, washed with ethanol and recrystallised from acetone yielding dark red shining needles, m.p. 199°, yield, 0.7 g. (41.7%).

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