Short Communication

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Substituted N-Methyl-N-Phenylhydrazones

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Treatment of quinoline-4- and quinoline-8-carboxaldehyde with a number of N-methyl-N-(nitro-substituted) phenyldrazines in absolute ethyl alcohol effected the formation of their N-methyl-N-phenyl-, N-methyl-N-*p*-nitrophenyl-, Nmethyl-N-2, 4-dinitrophenyl- and N-methyl-N-2,4,6-trinitrophenylhydrazones in 55.95% yield. Structural assignments of the products were characterized by their microanalyses, IR, ¹H-NMR and MS spectral data [1].

Attention has been recently begun to concentrate on the conjugated unsaturated ring systems containing nitrogen as biologically important compounds which may be active against the human immunodeficiency virus (HIV) and human cell representing major tumor types.

In view of their biological activity properties [2], we present here the synthesis of some typical hydrazones for the purpose of making contributions to said classes of substances.

The substrates quinoline-4-(1) and quinoline-8-carboxaldehyde (II) were reacted with equimolecular proportions of hydrazines. The reactions presented in the scheme, monitored by thin layer chromatography, proceed readily in absolute ethyl alcohol to give expected hydrazones in almost good yields (55-95%).



A reasonable approach to these reactions is known as nucleophilic attack of the requisite hydrazine on the corresponding aldehydes. In this way electronic and steric factors of reagent play a significant role in the success of the reaction and the reagents used in these reactions are a,b,c, and d which together form a series that the nitro groups on the ring have been systematically varied positions, condensation reactions of both substrates (I) and (II) rapidly occured with a which contains no nitro group. But the increasing number of the strong electron withdrawing nitro groups in the reagent gradually decreased the yield of the hydrazones.

In addition, the reactivities of substrates are significantly depended on the position of the carbonyl group in the quinoline system and increased by the presence of electronegative nitrogen atom relatively near to the carbonyl group. Therefore, of these two possible carbocationic centres, the one in the quinoline-8-carboxaldehyde was the more reactive. Thus, experimentally more effective results were obtained in the reactions of II. As a marked difference, condensation reactions of I were performed by use of the sulfuric acid and needed longer reaction time than II required. Furthermore, substrate I could be easily converted to its hydrate form ever though by the action of air. Consequently, formation of the

C=N-structures from I were carried out under strongly acidic conditions (pH=2) so that the carbonyl group of a less reactive substrate was made more reactive towards to these weak nucleophiles.

All these new hydrazones melt lower than the corresponding compounds derived from *p*-nitro-2,4-dinitro-,2,4,6trinitrophenylhydrazine and phenylhydrazine itself. This is in agreement with Franchimont's rule [3].

The structures assigned to the products are based upon microanalyses, IR, ¹H-NMR and MS. Results are summarized in Tables 1 and 2.

Comp.	Yield	Crystallized	M.P.(°C),	Molecular
No.	(%)	from	crystals	formula
Ia	95	Ethanol	1650°	C17H15N3
			Red needles	(261)
Ib	65	Ethanol	230°	C ₁₇ H ₁₄ N ₄ O ₂
			Yellow needles	(306)
Ic	66	Ethyl acetate/	271°	C, H, N, O,
		ethanol (1/1)	Pale yellow	(351)
Id	76	Ethanol/	246°	C, H, N, O,
		acetone (1/1)	Dense yellow	(396)
IIa	55	Ethanol	155°	C, ,H, ,N,
			Dense yellow	(261)
IIb	75	Methanol/	225°	C, H, N, O,
		acetone(1/1)	Orange needles	(306)
IIc	76	Acetone	235°	C, H, N, O,
			Orange bright	(351)
			needles	
IId	63	Acetone	205°	C, H, N, O,
			Orange-red	(396)

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Comp.	IR (KBr)	¹ H-NMR	MS m/e (M ⁺)	Analysis (%)		
No.	√[cm ⁻¹]	δ[ppm]		С	Н	N
				found	found	found
1941	ntohonn a ann marail a' se marailte ann ann ann ann ann	negari (negari) (negar	$x \geq \mu_{1} \geq h_{1} \geq h_{2}$	(calcd.)	(calcd.)	(calcd.)
Ia	3050, 1600, 1550, 1480,	3.70 (<u>s</u> , –NCH ₃ , 3H);	261	77.97	5.80	16.04
	1115, 860, 750, 685	7.05-8.96 (m, ArH and CH, 12H)		78.13	5.78	16.08
Ib	3030, 2900, 1590, 1550,	(CDCl ₃)	306	66.63	5.80	18.43
	1310, 1105, 960, 850,	3.67 (s, -NCH ₃ , 3H);		66.65	4.60	18.29
	750	7.43-8.99 (m, ArH and CH, 11H)				
Ic	3040, 2920, 1590, 1515,	(DMSO-d _e)	351	58.11	3.71	20.02
	1330, 1140, 960, 900	3.79 (<u>s</u> , -NCH ₃ , 3H);		58.12	3.73	19.93
	760, 740	7.61-8.95 (m, ArH and CH, 10H)				
Id	3100, 2980, 1605, 1535,	(DMSO-d ₆)	396	51.54	3.09	20.89
	1475, 1340, 1080, 910,	3.61 (s, -NCH ₃ , 3H);		51.52	3.05	21.20
	780, 710	7.75-9.12 (m, ArH and CH, 9H)				
IIa	3010, 2900, 1600, 1550,	(CDCl ₃)	261	78.25	5.62	15.92
	1495, 1110, 790, 750,	3.60, (s,-NCH ₃ , 3H); 6.95-		78.13	5.78	16.08
	690	9.10(m,ArH and CH 12H)				
IIb	3050, 2920, 1600, 1590	(CDCl ₃)	306	66.43	4.58	18.22
	1570, 1500, 1305, 1110	3.68(s,-NCH ₃ 3H); 7.44-		66.65	4.60	18.29
	835, 785, 750	9.13(m, ArH and CH, 11H				
IIc	3080,2920,1600,1580,	(CDCl ₃)	351	58.01	3.87	19.70
	1540,1500,1320,1150,	3.70(s-NCH ₃ , 3H);7.38-		58.12	3.73	19.93
	960,830,790,745	9.12 (m,ArH and CH, 10H)				
IId	3090,2950,1615,1545	(CDCl ₃)	396	50.96	3.06	20.84
	1525,1500,1330,1090,	3.51(s,-NCH ₃ , 3H);7.43-9.11		51.52	3.05	21.20
	970,830,800,720	(m, ArH and CH, 9H)				

TABLE 2. SPECTRAL DATA AND ELEMENTAL ANALYSES OF COMPOUNDS.

Elemental enalyses were obtained form Karl-Franzens University Laboratories Graz, Austria.

Compound I, m.p. 51-53°, and compound II, m.p. 93-94°, were produced from methylquinolines by oxidation with freshly prepared selenium dioxide [4-6]. Compound I was dehydrated by using sublimation apparatus, and II was obtained by maintaining final oxidation temperature at 220° instead of 250° to avoid formation of 8-quinolinecarboxylic acid. Reagents a-d were prepared as descirbed [7-9]. Reagent N-methyl-N-phenylhydrazine was redistilled under vacuum immediately prior to use. All of these substrates and reagents were characterized by their IR, ¹H-NMR spektral data, boiling and melting point comparisons with the reported literature values [5,7-9].

Preparation of N-methyl-N-phyenylhydrazones 1 a-d and II a-d; General procedure. Compound I or II (0.95 mmol) is dissoslved in hot absolute ethanol (5 ml) and an equimolar amount of reagent a-d, dissolved in a minumum volume of absolute ethanol, is added. The reacton mixture is refluxed till the colour turns and then allowed to cool to room temperature. Formed crystalline precipitate is suction collected and airdried. Further crystallizations of the crude product gives an analytical sample of hydrazone.

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Key words: Condensations, N-methyl-N-phenylhydrazones, Quinolinecarboxaldehydes.

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