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An expedient synthesis and spectral studies of novel substituted phenyl anilic acid hydrazides and their acid hydrazones

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ABSTRACT

Rapid and efficient procedure for the preparation of acid hydrazones by the condensation reactions of 3-chloro-4-methoxy & 2-methoxy-5-methyl malon anilic acid hydrazides with different substituted aldehydes and ketones. The newly synthesized compounds have been characterized by analytical analysis and spectral studies like IR.

Key words:

INTRODUCTION

The Introduction of various functional grou ps in acid hydrazide and it's derivatives has led to the discovery of compounds like isonicotinic acid hydrazide , with enhanced antibacterial pr operties along with a decrease in toxicity . The introduction of sulfonyl group in various hydraz ides was found to increase the reactivity of the parent compound[1,2]. Isonicotinic acid hydrazi de[3] and it's derivatives are effective drugs in th e treatment of human tuberculosis , tuberculos tatic activity of it's reaction products with various aldehydes and ketones is well known [4-5]. Acid hydrazides have also been found to pos sess potential anti-bacterial[6-7], antifungal[8], anti-tumor and anti-diabetic[9],analgesic[10] activities.

A large number of acid hydrazones have be en reported to possess bactericidal[11] properties. Hydrazones have also been found to posse ss antibacterial[12],antifungal[13],antiviral[14], insecti cidal[15] activity, Isatin hydrazones is suitable as reagents in the determination of 3-ketosteroids, it have also gained commercial significance as electrical insulators, coating,adhesives and I nks.In this laboratory,a large number of acid hy drazides and acid hydrazones have been synth esized by various workers[16-19]. As a continuati on of our previous studies on the synthesis of malonamic acid hydrazides and their acid hydr azones[20].

In this synthesis of the paper ,we report the condensation of phenyl anilic acid hydrazides with different substituted aromatic aldehydes and ketones. The condensation took place readily in alcoholic medium and 16 new acid hydraz ones were prepared.

EXPERIMENTAL

Material

Melting points were taken in open capi llary tubes and are uncorrected . All chemicals are used in the synthesis were obtained from Sigma-Aldrich company .All of the compounds were recrystallised by absolute ethanol 99.9%.

The purity of newly synthesized compounds we re checked by TLC on silica-gel-coated Al Plat es (E-Merck) by using 20% benzene/ methanol as developing solvent.

The IR spectra in Kbr were recorded on a Perkin-Elmer RX-1 FT-IR spectrophotometer at St. John's College Agra. The physical properties and analytical data of the synthesized compounds were listed in Table-1.

Synthesis of N(R)-phenyl malon acid hydra zides (1a,2a)

The substituted amine (3-chloro-4-methoxy,2-methoxy-5-methyl;0.025 mole) and diethyl malonate (0.05 mole) was added with a catalyst (DMF) and then refluxed for 45-60 min utes, after cooling,ethanol (20ml) was added ,filtered ,and then concentrated over a boiling water-bath,after cooling,add ethyl alcohol (20 ml) and hydrazine hydrate 99%, after some time the solid separated , was recrystallised by hot ethanol ,and was identified N-(R)-phenyl malon-anilic acid hydrazides(1a,2a).

Synthesis of acid Hydrazones(3a-3h,4a-4h)

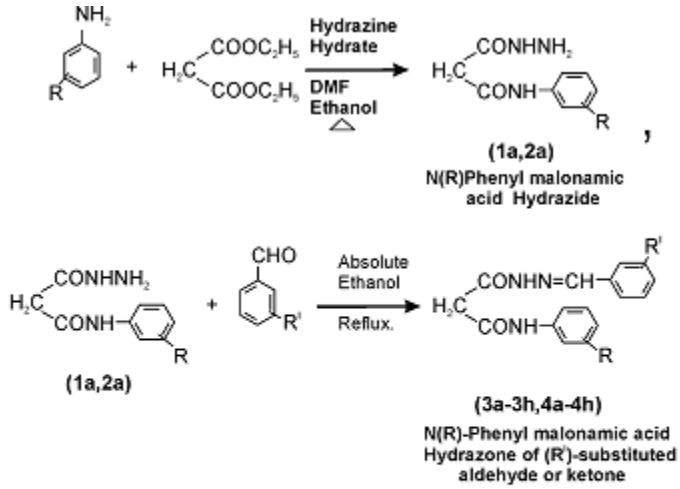
To (1a,2a;0.001 mole) dissolved in absolute ethanol (10 ml) and (R^{I}) substituted aldehyde or ketone (0.001 mole) was refluxed for 2 hours, the solid obtained on cooling, filtered, was recrystallised by absolute ethanol se veral times,and was identified to be N-(R) phenyl malonamic acid hydrazone of (R^{I})sub stituted aldehydes or ketones (3a-3h,4a-4h).The structures of acid hydrazides and acid hydrazones are furnished in the following manner.

(R)= 3-chloro-4-methoxy,2-methoxy-5-methylaniline

RESULTS AND DISCUSSION

The Infrared spectra in KBr of the synthesized acid hydrazides and acid hydrazones have been reported in the frequency region 4000-450 Cm^{-1}, in the Table 2.

The IR spectrum of N-(3-chloro-4-methoxy) ph enyl malonamic acid hydrazone of 4-hydroxy benzaldehyde [3a] show -CONH stretching vibrations at 1637.1 cm^{-1},absorption at 3439.9 cm^{-1} in dicates -NH stretching vibrations,-N=CH stretc hing vibrations at 2360.8 Cm^{-1},absorption at 67 0.5 cm^{-1} indicates -C-Cl stretching vibrations a nd the IR spectrum of N-(2-methoxy-5-methyl) phenyl malonamic acid hydrazone of 2-Hydroxy-1-Naphthaldehyde[4a] indicates -CONH stret ching vibrations at 1685.9 cm^{-1}, absorption at 3414.5 cm^{-1} reveals -NH stretching vibrations, absorption at 2367.6 cm^{-1} indicates -N=CH str etching vibrations,-C-Cl stretching vibrations at 668.6



R^{I}	- 4-Hydroxy Benzaldehyde	(3a)	R^{I}	- 2-Hydroxy-1-Naphthaldehyde	(4a
	- 2-Nitro Benzaldehyde	(3b)		- Vaniline	(4b
	- 4-Methoxy Benzaldehyde	(3c)		- P-Methoxy Benzaldehyde	(4c
	- 3,5-Dichloro Salicylaldehyde	(3d)		- Acetone	(4d
	- 2-Hydroxy-1-Naphthaldehyde	(3e)		- P-Chloro Benzaldehyde	(4e
	- Acetone	(3f)		- Acetophenone	(4f
	- 5-Chloro Salicylaldehyde	(3g)		- Furfuraldehyde	(4g
	- Ethyl methyl ketone	(3h)		- Ethyl methyl ketone	(4h

Table 1 : Analytical & Physical data of the Synthesized Compounds (1a,2a,3a-3h,4a-4h)

S. No.	Compounds code	Molecular Formula	Molecular Weight	Melting Point 0°C	Yield %	Colour	% Analytical data					
							C cal.%	(Found)	H cal.%	(Found)	N cal.%	(Found)
1.	1a	$C_{10}H_{12}N_3O_3Cl_1$	257.68	158°	56.30	White	46.61	(46.65)	4.69	(4.70)	16.30	(16.33)
2.	2a	$C_{11}H_{15}N_3O_3$	237.26	129°	44.23	White	55.68	(55.72)	6.37	(6.38)	17.71	(17.75)
3.	3a	$C_{17}H_{17}N_3O_4Cl_1$	362.80	144°	33.77	raw silk	56.28	(56.30)	4.72	(4.73)	11.58	(11.60)
4.	3b	$C_{17}H_{16}N_4O_5Cl_1$	391.79	211°	42.64	white	52.11	(52.12)	4.11	(4.12)	14.30	(14.33)
5.	3c	$C_{18}H_{19}N_3O_4Cl_1$	376.83	188°	52.41	white	57.37	(57.39)	5.08	(5.10)	11.15	(11.17)
6.	3d	$C_{17}H_{15}N_3O_4Cl_3$	431.70	180°	42.63	light cream	47.30	(47.32)	3.50	(3.51)	09.73	(09.75)
7.	3e	$C_{21}H_{19}N_3O_4Cl_1$	412.86	231°	39.16	cream caress	61.09	(61.12)	4.64	(4.63)	10.18	(10.21)
8.	3f	$C_{13}H_{15}N_3O_3Cl_1$	296.73	92°	38.05	liley pad	52.62	(52.63)	5.09	(5.11)	14.16	(14.19)
9.	3g	$C_{17}H_{16}N_3O_4Cl_2$	397.25	242°	47.45	white	51.39	(51.42)	4.06	(4.08)	10.58	(10.60)
10.	3h	$C_{14}H_{19}N_3O_3Cl_1$	312.78	84°	31.00	light cream	53.76	(53.78)	6.12	(6.14)	13.43	(13.45)
11.	4a	$C_{22}H_{22}N_3O_4$	392.44	218°	46.21	wild yellow	67.33	(67.35)	5.65	(5.66)	10.71	(10.70)
12.	4b	$C_{19}H_{22}N_3O_5$	372.41	165°	44.47	jasmine	61.27	(61.26)	5.95	(5.97)	11.28	(11.30)
13.	4c	$C_{19}H_{22}N_3O_4$	356.41	178°	83.64	white	64.03	(64.05)	6.22	(6.24)	11.79	(11.81)
14.	4d	$C_{14}H_{19}N_3O_3$	277.32	132°	35.90	broken white	60.63	(60.65)	6.90	(6.91)	15.15	(15.17)
15.	4e	$C_{18}H_{19}N_3O_3Cl_1$	360.83	214°	38.90	cream	59.91	(59.90)	5.30	(5.31)	11.64	(11.67)
16.	4f	$C_{19}H_{22}N_3O_3$	340.41	186°	46.49	white	67.04	(67.06)	6.51	(6.53)	12.34	(12.37)
17.	4g	$C_{16}H_{18}N_3O_4$	316.34	201°	52.55	dawn	60.75	(60.77)	5.73	(5.75)	13.28	(13.30)
18.	4h	$C_{15}H_{22}N_3O_3$	292.36	121°	40.12	blue bell white	61.62	(61.64)	7.58	(7.59)	14.37	(14.39)

Table 2: Infrared absorption bands

S. No.	Compounds code	-CONH cm^{-1} stretching	-NH cm^{-1} stretching	-N=CH cm^{-1} stretching	-C-Cl cm^{-1} stretching
1.	3a	1637.1	3439.9	2360.8	670.5
2.	3b	1680.4	3438	2362.1	669.6
3.	3c	1651.2	3421.6	2361.4	670.2
4.	3d	1652.8	3426	2361.2	6702
5.	3e	1654.8	3469.8	2361.8	670.2
6.	3f	1684.4	3425	2362.4	669.1
7.	3g	1661.7	3452.2	2362.2	669.9
8.	4a	1685.9	3414.5	2367.6	668.6
9.	4b	1654.2	3414.5	2362.4	668.4
10.	4c	1654.7	3419.9	2362.3	668.5
11.	4d	1653.9	3448	2362.1	668.5

Cm^{-1}.These infrared absorption observations are support to assigned structure of co mpounds no. 3a,4a. All the above observations of newly synthesized compounds are agreed with assigned structure of compounds no. 3b-3g&4b-4d and other compounds no.(3h&4e-4h).

REFERENCES

1. H. Zimmer, B.H. Gross, E.H. Geriach, K. Fry, A.C. Promay & H. Schmank., *J. Org. Chem.*, **24**: 1667 (1956).
2. A.A. Munshi, N.M. Shah & J.P. Trivedi., *Indian. J. Chem.*, **1**: 311 (1963).
3. H.H. Fox, *J. Org, Chem.*, **17**: 542 (1952).
4. Hoggarth, Martin, Storey & Young, *Brit. J, Pharmacol.*, **4**: 248 (1949).
5. Donovick, Pansy, Stryker & Bernstein, *J. Bacterial.*, **59**: 667 (1950).
6. A.K. Sengupta, M.M.Gupta and A.A. Gupta, *J. Indian Chem. Soc.*, **61**: 643 (1984).
7. A.A. Martijnovskii, A.A.Brazhko and E.N. Luschinskaya (Zaporozh. Med.Inst., Zaprozhe ,USSR) *Farm. Zh* (Kiev), **8**: 62-64 (Ukrain) (1986).
8. O.H. Hishmat, S.S. Mabrouki, A.M.M. Nassef, N.M. A.Shayeb and S.A. Ismail (*Nat. Proct, Dep., Natt, Res. Cent. Cairo, Egypt*) *Egypt. J. Pharm. Sci*, **30**(1-4): 133-43 (1989); **112**: 157979c (1990).
9. V.P. Chemykn, V.I. Makurina, I.N. Timashwa, L.N. Voroinina, Z.S. Spesivtseva, L.D. Khaleeva and P.A.Petyonin (*KharkovPharm. Ins t., Kharkov*, USSR) *Farm.Zn. (Kiev)* **6**: 47-50 (1978); C.A, **90**: 203649Z (1979).
10. I.S.Berdinskii,L.V.Kasakova,A.f.Golenw and E.L.Pidemskii (*Pharm,State.Univ.*) USSR, 650, 996 (Cl.C07C109/06) 5 March (1979) C.A., **90**: 1866025J (1979).
11. Mehboob Sardar and M.L. Dhar, *J. Sci. Ind. Res.*, **1**: 146 (1955).
12. R.H. Wiley and R.L.Clevenger, *J. Med. Pharm., Chem,* **5**: 1367-71 (1962).
13. A. Margot and H.Gysin, *U.S. Patent*, **2**: 740,762 (1956).
14. K. Dimitriji, I.Bavic, S.Cvetnic and A.Deljac, *Acta.Pharm.*, Jugosl, **25**(4): 241-46 (1975).
15. G.T. Bottger, A.P.Yerington and S.I.Gertler, U.S. Deptt., *Agr. Bur. Entomol and Plant Quarantine*, E-815: 17 (1951).
16. O.P. Singhal and P.I. Ittyerah, *Indian. J. Appl. Chem.*, **29**: 89 (1966).
17. A.K. Mittal and O.P.Singhal, *J. Indian. Chem. Soc.*, L**XIII**: 759-60 (1986).
18. M. Kalani, *Ph.D.Thesis, AgraUniv.*, Agra (1989).
19. K.Ghosh, *Ph.D.Thesis*, *AgraUniv.*, Agra (2002).
20. Alok K. Pareek, P.E. Joseph and Daya S. Seth., *Orient.J.Chem.*, **25**(1): 159-163 (2009).