

NOTE**Synthesis of Hydrazones of Stobbe Acid and its Rearranged Products**

JOLLY JACOB, M.A. DAVE* and S.N. PARASHAR

Department of Chemistry, K.J. Somaiya College of Science and Commerce
Vidya Vihar, Mumbai-400 077, India
E-mail: sandhya@somaiya.com

Stobbe anhydride (**I** and **II**) was condensed with diazonium salts of various aromatic amines to form hydrazones or dyes [**I** and **II** (**a–c**)] which were further treated with nucleophiles like 10% NaOH and NaBH₄ to give various pyrazolinone [**I** and **II** (**d–f**)], [**I** and **II** (**g–i**)] and cyclic imide [**I** and **II** (**j–l**)] derivatives.

Key Words: Stobbe acid anhydride, Nucleophiles.

Stobbe acid system contains an active methylene group due to which it could be subjected to azo-coupling reactions for synthesis of hydrazone^{1,2}, which further provide an active centre for a number of nucleophilic reactions. Literature survey reveals that cyclic anhydrides having an active methylene group are convenient starting materials that can yield the derivatives of pyridazines^{3,4} and pyridones possessing some bioactivity. The azo-coupling reaction having active methylene compound produces the corresponding hydrazones^{6–8}. The synthesis of stobbe anhydride (**I** and **II**) and the condensations of (**I** and **II**) with diazonium salt to give stobbe hydrazones^{9,10} [**I** and **II** (**a–c**)] have been reported. These hydrazones synthesized were subjected to various nucleophilic reactions.

In the present paper, a variety of dyes, *i.e.*, hydrazones were prepared by condensation of 3-phenoxy stobbe anhydride (**I**) and 3,4-dimethoxy stobbe (**II**) anhydride with different aryl diazonium chloride salts.

Since the azo dyes prepared have their α -position substituted by a hydrazone group, it was thought worthwhile to carry out similar type of reactions to give pyrazolone derivatives¹¹ and cyclic amides.

General procedure for synthesis of anhydride of stobbe acid

To a solution of Stobbe acid (0.002 mol) in dry chloroform redistilled acetyl chloride was added. The reaction mixture was refluxed on a water bath for about 3 h. Excess of chloroform and acetyl chloride was removed by distillation. An anhydride formed as crystallized from suitable solvent.

General procedure for synthesis of hydrazones

Aromatic amine (0.002 mol) was dissolved in 6 N HCl and was diazotized by dropwise addition of aqueous NaNO₂ solution (0.002 mol) at 0°C with stirring. This was then added dropwise to a solution of stobbe anhydride (0.0014 mol) in acetone at 10°C with constant stirring. The reaction mixture was stirred for 30 min till an orange coloured solid separated out. About 50 mL of water was added

to it and then the dye was filtered. It was washed with water, dried and crystallized from suitable solvent.

The melting and analytical characteristics of the synthesized compounds are given in Table-1 ¹H NMR spectra were recorded on a Varian VXR-300SH (300 MHz) NMR spectrometer using DMSO-d₆ as solvent and TMS as internal standard.

TABLE-1
PHYSICAL DATA OF THE COMPOUNDS

Compd. No.	m.f.	m.p. (°C)	Yield (%)	IR (cm ⁻¹)	UV (nm)
I	C ₁₇ H ₁₄ O ₄	68	81.00	1789, 1651	—
II	C ₁₃ H ₁₂ O ₅	170	93.00	1767, 1707	—
Ia	C ₂₅ H ₂₀ N ₂ O ₄	138	50.41	3219, 1657, 1641	305, 335
Ib	C ₂₃ H ₁₆ N ₂ O ₄ Cl	145	50.19	3269, 1810, 1671	—
Ic	C ₂₄ H ₁₈ N ₂ O ₄	136	53.94	3285, 1709, 1668	—
IIa	C ₂₁ H ₂₀ O ₅ N ₂	165	67.21	2916, 1707, 1760	319
IIb	C ₁₉ H ₁₅ N ₂ O ₅ Cl	175	54.42	2917, 1769, 1710	292, 316
IIc	C ₁₉ H ₁₆ O ₅ N ₂	158	80.00	2925, 1765, 1706	281, 310
Id	C ₂₅ H ₂₀ N ₂ O ₄	182	67.96	1703, 1636	275
Ie	C ₂₃ H ₁₅ N ₂ O ₄ Cl	176	86.60	1703, 1637	—
If	C ₂₄ H ₁₈ N ₂ O ₄	182	82.91	1702, 1637	—
IIId	C ₁₉ H ₁₆ O ₅ N ₂	185	60.12	1708, 1669	228, 311
IIe	C ₁₉ H ₁₅ O ₅ N ₂ Cl	156	63.25	1707, 1669	287, 310
IIIf	C ₂₁ H ₂₀ O ₅ N ₂	186	60.05	1705, 1669	283, 311
Ig	C ₂₅ H ₂₂ N ₂ O ₃	90	33.08	3440, 1701, 1637	285
Ih	C ₂₃ H ₁₆ N ₂ O ₄ Cl	88	52.10	3421, 1710, 1671	—
Ii	C ₂₄ H ₂₀ N ₂ O ₃	92	45.74	3449, 1655, 1624	—
IIg	C ₂₁ H ₂₂ O ₄ N ₂	99	68.01	3427, 1679	295, 326
IIh	C ₁₉ H ₁₇ O ₅ N ₂ Cl	120	61.18	3433, 1667	232, 313
IIi	C ₁₉ H ₁₈ O ₄ N ₂	95	57.12	3328, 1671	—
Ij	C ₃₁ H ₂₅ N ₃ O ₃	168	86.41	3286, 1667	235, 265
Ik	C ₂₉ H ₂₀ N ₃ O ₃ Cl	168	89.50	3288, 1681	—
II	C ₃₀ H ₂₃ N ₃ O ₃	165	87.47	3289, 1668	—
IIj	C ₂₇ H ₂₅ O ₄ N ₃	180	62.00	2919, 1703, 1649	298, 335
IIk	C ₂₅ H ₂₀ O ₄ N ₃ Cl	195	59.10	2923, 1704, 1649	296, 329
III	C ₂₅ H ₂₁ O ₄ N ₃	178	65.61	2982, 1673, 1635	289, 313

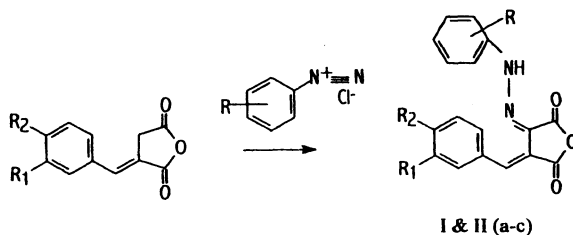
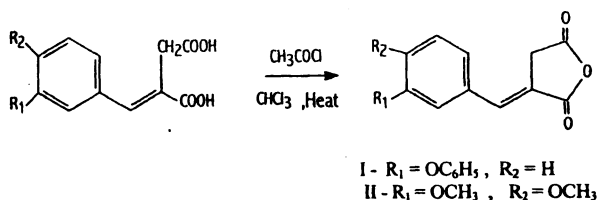
General procedure for synthesis of pyrazolone (III)

Reaction of hydrazone with 10% NaOH (II-d-f): A mixture of 10% NaOH and stobbe hydrazone 0.001 mol was refluxed for 2 h. The clear solution obtained was cooled and acidified with 1 : 1 HCl; when a solid separated out, it was filtered, washed with water and crystallized from suitable solvent.

Reaction of hydrazone with sodium borohydride (IIg-i): Sodium borohydride 0.00025 mole was added to a suspension of stobbe hydrazone 0.001 mol in methanol. The mixture was stirred at room temperature vigorously. The clear solution obtained was acidified with 1 : 1 HCl; when a solid separated out, it was washed with water and crystallized with suitable solvent.

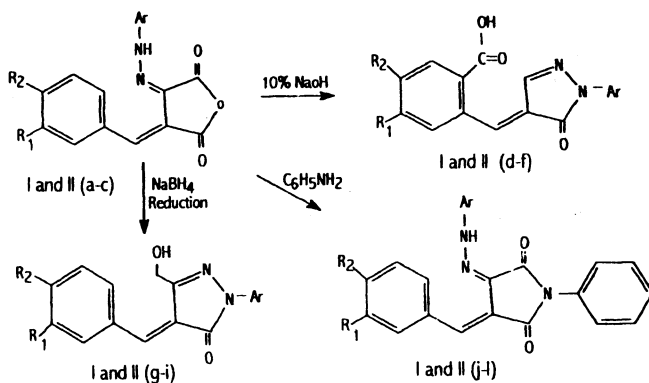
Reaction of hydrazone with amine (IIj-l): Stobbe hydrazone was refluxed with amine 0.001 mol in ethanol for 4 h on a water bath. Ethanol was distilled off and water was added to the residue obtained; the solid separated was filtered, washed with water and crystallized with suitable solvent.

Synthetic strategy has been outlined below:



Ia - $\text{R}_1 = \text{OC}_6\text{H}_5$, $\text{R}_2 = \text{H}$, R = 2,6-dimethyl
 Ib - $\text{R}_1 = \text{OC}_6\text{H}_5$, $\text{R}_2 = \text{H}$, R = 3-Cl
 Ic - $\text{R}_1 = \text{OC}_6\text{H}_5$, $\text{R}_2 = \text{H}$, R = 4-CH₃

IIa - $\text{R}_1 = \text{OCH}_3$, $\text{R}_2 = \text{OCH}_3$, R = 2,6-dimethyl
 IIb - $\text{R}_1 = \text{OCH}_3$, $\text{R}_2 = \text{OCH}_3$, R = 3-Cl
 IIc - $\text{R}_1 = \text{OCH}_3$, $\text{R}_2 = \text{OCH}_3$, R = 4-NO₂



Ia: A singlet occurring between δ 3.2 ppm to δ 3.4 ppm may be due to the methylene protons. A broad multiplet in the region of δ 7.0 ppm to δ 7.7 ppm could be assigned to the protons (^{13}H) attached to the benzene ring.

Id: A singlet occurring between δ 3.2 ppm to δ 3.6 ppm may be due to the methylene protons. A multiplet in the region of δ 7.0 ppm to δ 7.8 ppm could be assigned to the protons (^{13}H) attached to the benzene ring. The broad signal at δ 126 ppm may be due to carboxylic proton.

REFERENCES

1. F. Henrich and T. Thomas, *Ber*, **40**, 4924 (1907).
2. B.A. Limaye and V.M. Bhave, *J. Indian Chem. Soc.*, **77**, 403 (1931).
3. D.S. Kanekar, S.D. Samant, S.R. Pendnekar, S.D. Deval and K.D. Deodher, *Indian J. Chem.*, **20B**, 998 (1981).
4. S.R. Pendnekar, Ph.D. Thesis, University of Mumbai (1983).
5. K.D. Deodher and S.D. Deval, *Synthesis*, 421 (1983).
6. R.A. Parent, *J. Soc. Dyer, Colourist*, **78**, 368 (1976).
7. S.M. Parameter, *Org. Reaction*, **10**, 1 (1959).
8. T. Zinke and H. Bindewald, *Ber*, **17**, 3026 (1884).
9. M. Malachowki and M. Giedroyo, *Ber*, **61**, 2527 (1928).
10. M.I. Ali, A. El-Sayed and A.M. Abdul. Fattah, *Indian J. Chem.*, **15B** (1980).
11. L. Korr, *Ber*, **16**, 2597 (1883); **17**, 2037 (1884); *Ann.*, 238, 137, 203 (1887).

(Received: 21 June 2004; Accepted: 3 November 2004)

AJC-4092