# ANALYTICAL DATA

# CONDENSATION OF SOME SUBSTITUTED SALICYLALDEHYDES WITH HYDRAZINE

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Summary—Hydrazones and azines of 5-chloro-, 5-bromo-, 3,5-di-iodo-, 5-nitro- and 3-nitro- salicylaldehydes have been prepared by condensation with hydrazine. They have been characterized by their melting points, solubilities, elemental analysis and infrared spectra. Ambiguous literature on some of the compounds has also been clarified. Conditions for smooth condensation have been worked out. The extent of the condensation is found to depend on the nature of the substituent group in the salicylaldehydes.

Hydrazones in general are prepared by refluxing the stoichiometric amounts of the appropriate hydrazine and aldehvde (or ketone) dissolved in a suitable solvent. The reaction with substituted (phenyl-, p-nitrophenyl- and 2,4-dinitrophenyl-) hydrazines is extensively used in detection, determination and isolation of carbonyl compounds. Some substituted hydrazones<sup>1,2</sup> have been used in analysis and in the study of human and plant physiology but as we pointed out earlier,<sup>3</sup> the condensation of aromatic aldehydes with hydrazine to prepare hydrazones is difficult because of formation of the more stable azines, which is the main reason for the meagre and ambiguous literature on the hydrazones and azines. Though some of the azines<sup>4-8</sup> have been prepared and studied, very little work has been done on hydrazones.<sup>8-11</sup>

In the present study some substituted salicylaldehydes were prepared and condensed with hydrazine to yield the corresponding hydrazones or azines. Some compounds hitherto not mentioned in the literature have been isolated and characterized. An attempt has also been made to resolve the ambiguities in the literature on some of the known condensation products.

#### EXPERIMENTAL

5-Chloro-, 5-bromo-, 3,5-di-iodo-, 5-nitro- and 3-nitrosalicylaldehyde were prepared by standard methods. $^{12-14}$ 

### Formation of hydrazones

These were prepared by slowly adding 0.1 mole of substituted salicylaldehyde (dissolved in alcohol) to 0.1 mole of hydrazine hydrate in 50 ml of alcohol. A slight excess of hydrazine hydrate was used to avoid the formation of azine. The mixture was shaken thoroughly after each addition, refluxed for an hour on a water-bath and cooled; the hydrazone then separated. The products were recrystallized from methyl alcohol as crystalline needles.



X is the substituent group in the salicylaldehyde.

#### Formation of azines

These were prepared by slowly adding 0.1 mole of hydrazine hydrate to 0.2 mole of substituted salicylaldehyde dissolved in alcohol, refluxing on a water-bath for half an hour and then cooling. The product was filtered off and washed with alcohol. The salicylaldazines were obtained (as powders) in good yields.





All the azines are practically insoluble in common polar organic solvents, sparingly soluble in non-polar organic solvents and aqueous ammonia but soluble in alkalis.

The identity of the compounds was established by elemental analysis and infrared spectroscopy. The hydrazones and azines were distinguished by the difference in their melting points and solubilities. Their characteristics are summarized in Table 1.

## **RESULTS AND DISCUSSION**

The reaction of aliphatic aldehydes with hydrazine is so rapid that the hydrazones formed as intermediate products cannot be isolated, and even in

Substituent	*Hydrazones			Azines	
	m.p., °C	Colour	Solubility	m.p., °C	Colour
5-chloro	84	white	A	288	yellow
5-bromo	80	white	Α	305	yellow
5-nitro	186	vellow	В	> 300	vellow
3-nitro	175	vellow	В	> 300	orange-vellow
3,5-di-iodo	196	yellow-white	Α	> 300	yellow

Table 1. Characteristics of substituted salicylaldehyde hydrazones and azines

\* A-soluble in common organic solvents and alkalis, but insoluble in acids.

B---soluble in most polar organic solvents, ammonia and alkalis, but practically insoluble in non-polar organic solvents and acids.

presence of excess of hydrazine the azines are practically the only products. However, the aromatic hydrazones can be readily isolated by using a slight excess of hydrazine. Though salicylaldehyde hydrazone<sup>8-11</sup> and salicylaldazine<sup>4-6</sup> have been prepared and their metal complexes studied, very little work has been done on the condensation of substituted salicylaldehydes and hydrazine. Patwardhan et al.7 have reported on the Ti(IV) chelates of azines prepared from 5-chlorosalicylaldehyde and 5-bromosalicylaldehyde but gave details only for salicylaldazine. Torrey and Brewster<sup>4</sup> prepared and studied hydrazones of oxyaldehydes and ketones, but found only azines when hydrazine was used. At 100° 5-bromosalicylaldazine changes colour from pale yellow to orange, and this was confused with its melting point in the chemical abstract, though the original paper says the compound sinters at 301° and decomposes at 305-307°.

Likewise, the only hydrazone of a substituted salicylaldehyde mentioned in the old literature<sup>15</sup> is 3,5-di-iodosalicylaldehyde, which is said to decompose at 200°. The same m.p. (200°) is given for 3,5-diiodosalicylaldazine in Beilstein.<sup>16</sup> Our work shows that the hydrazone decomposes at 196°, but the azine is stable up to 300°.

In optimization of the formation of hydrazones and azines, it has been found that for the former, the substituted salicylaldehyde should be added to the hydrazine, and for the latter, the order should be the reverse, *i.e.*, hydrazine should be added to the substituted salicylaldehyde. The reaction is exothermic and dropwise addition is therefore required, with either cooling or sufficient dilution with alcohol to carry out the reaction smoothly. The contents may then be refluxed on the water-bath. The hydrazones and azines are separated by taking advantage of the fact that only the former are appreciably soluble in alcohol.

The extent of reaction appears to depend on the nature of the substituent group. An electron-attracting group (nitro- or halo-) is more favourable than an electron-releasing group for the formation of hydrazones. This agrees with the observations of Rao and Ratnam<sup>17</sup> on formation of mono-and di-substituted benziminazoles by the condensation of *o*-phenylene diamine and substituted aromatic aldehydes.

#### REFERENCES

- 1. M. Katyal and Y. Dutt, Talanta, 1975, 22, 151.
- M. Katyal and W. A. E. McBryde, *Technical News Service*, Vol. X, Nos 1 and 2, Sarabhai M. Chemicals, Baroda, India, 1978.
- 3. M. P. Jain and S. Kumar, Talanta, 1977, 24, 149.
- 4. H. A. Torrey and C. M. Brewster, J. Am. Chem. Soc., 1913, 35, 426.
- 5. C. S. Marvel and P. V. Bonsignore, *ibid.*, 1959, **81**, 2668.
- S. Satapathy and B. Sahoo, J. Inorg. Nucl. Chem., 1970, 32, 2223.
- 7. H. A. Patwardhan, S. Gopinathan and C. Gopinathan, Indian J. Chem., 1978, 16A, 224.
- 8. L. Hunter and J. A. Marriott, J. Chem. Soc., 1937, 2000.
- 9. H. L. Ray, Ph.D. Thesis, 1973, Delhi University, Delhi.
- H. L. Ray, B. S. Garg and R. P. Singh, J. Chin. Chem. Soc., 1976, 20, 47.
- 11. M. P. Jain and S. Kumar, Indian J. Chem., 1978, 16A, 464.
  - 12. H. Biltz and K. Stepf, Ber., 1904, 37, 4022.
  - 13. J. Bougault, E. Cattelain, P. Chabrier and A. Quevauviller, Ann. Pharm. France, 1949, 7, 163.
  - 14. W. von Miller, Ber., 1887, 20, 1927.
  - 15. Abstracts of Chemical Papers, 1898, 368.
  - Beilstein, Handbuch der Organischen Chemie, 4th Ed., Vol. VIII, p. 56. Springer, Berlin, 1925.
  - N. V. Subba Rao and C. V. Ratnam, J. Ind. Chem. Soc., 1961, 38, 631.