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ON THE CONDENSATION OF SALICYLALDEHYDE WITH HYDRAZINE

EMMANUEL CHUKWUEMEKA OKAFOR
Department of Chemistry, University of Nigeria, Nsukka, Anambra State, Nigeria

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Summary—A simple procedure for preparing uncontaminated salicylaldehyde hydrazone is outlined. The condensation reaction of salicylaldehyde and hydrazine in 2:1 molar ratio usually gives initially a mixture of the three geometrical isomers of salicylaldazine: one isomer is bright yellow, another is cream, the third is light pink. The earlier reports of Feigl and of Terentev *et al.* on the use of salicylaldehyde in the detection of hydrazine have been found to be misleading and the later report of Jain *et al.* incomplete. A detailed account is now given and improved salicylaldehyde tests for hydrazine are recommended. The structure given by Jain *et al.* for the copper(II) complex of salicylaldehyde hydrazone is confirmed by means of infrared spectroscopy and microanalysis. Preliminary studies on the copper(II) complex of salicylaldazine are reported.

Some confusion appears to have arisen about the condensation reaction of salicylaldehyde with hydrazine which is the basis of the salicylaldehyde test for hydrazine as described by Feigl.[1] Jain *et al.*[2] attributed the earlier misleading and confused reports on hydrazones to the fact that it is difficult to prepare hydrazones from hydrazine, because they tend to react further, giving azines.[3]. They further reported that the condensation of salicylaldehyde with hydrazine gives two different compounds: salicylaldehyde hydrazone (SH), $HO{\cdot}C_6H_4CH = N{\cdot}NH_2$ (shiny white plates, m.p. 97.5°) and salicylaldazine (SA), $HO{\cdot}C_6H_4{\cdot}CH = N{\cdot}N = CH{\cdot}C_6H_4OH$ (shiny yellow plates, m.p. 210°, literature value[4] 208–210°, 213–214°, 216°).

Our detailed studies reveal that it is not too difficult to prepare SH from hydrazine provided the following points are noted.

(*i*) Salicylaldehyde has to be added to hydrazine and the molar ratio of the reactants should be 1 : 1. Adding hydrazine to salicylaldehyde means that salicylaldehyde is initially in excess and some azine would be formed.

(*ii*) Fairly dilute ethanolic solutions of both reactants should be used.

(*iii*) The salicylaldehyde solution has to be added slowly and with stirring

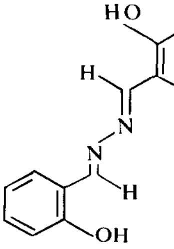
The reaction is exothermic and creamy white flakes crystallize from the reaction mixture on cooling (m.p. 93–95°). No heating is necessary.

When one mole of ethanolic solution of hydrazine hydrate is added to two moles of ethanolic salicylaldehyde solution at room temperature a mixture of the three geometrical isomers of salicylaldazine is usually obtained. The reaction is exothermic and no heating is required. In the course of our studies[5] we have isolated and identified the three geometrical isomers: Isomer A crystallizes as bright yellow needles from acetone (m.p. 222–223°); isomer B is light pink (m.p. 220°); isomer C is cream (m.p. 220°). Isomer B is not as stable as the other two. It transforms into the cream form at room temperature (~25°) after about 12 hr.

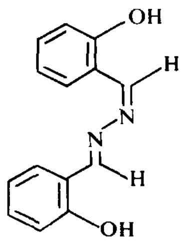
Feigl,[1] in describing a test for hydrazine with salicylaldehyde, claimed that "Benzaldehyde and other aromatic aldehydes condense with hydrazine and its salts to form water-insoluble colourless aldazines. Owing to its greater solubility in water salicylaldehyde is specially useful as a specific reagent." Jain *et al.*[2] have reported that he is mistaken, that the white compound formed is salicylaldehyde hydrazone, and that salicylaldazine is yellow. However, these authors have not realized that there are three possible geometrical isomers of salicylaldazine, which do in fact exist. Our detailed study reveals the following.

(1) The order of addition of reagents is extremely important. If ethanolic salicylaldehyde (2 mole) is added gradually with stirring to hydrazine hydrate (1 mole), some whitish product can be observed, owing to the formation of some hydrazone, but if the order is reversed as it should be, and ethanolic hydrazine is added to ethanolic salicylaldehyde, then at room temperature a mixture of the geometrical isomers is initially obtained; if the reaction mixture is heated on a water-bath for about 1 hr, the yellow isomer is obtained as the only product.

(2) Feigl's report[1] that aromatic aldehydes form colourless azines with hydrazine is not true. The most stable geometrical isomer, which is usually the most abundant, is generally yellow or cream in colour, as shown by the following azines prepared in our laboratories.



A



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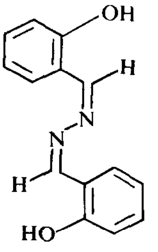


C

(*i*) Salicylaldazine (isomer A bright yellow, m.p. 222–223°); (isomer B light pink, m.p. 220°); (isomer C cream, m.p. 220°).

(*ii*) *p*-Anisalaldazine (isomer A yellow, m.p. 173°).

(*iii*) Cinnamaldehyde azine (isomer A orange, m.p. 176–178°).

(*iv*) *p*-Methylbenzaldazine (isomer A light yellow, m.p. 160–161°).

(*v*) Benzaldazine (isomer A yellow, m.p. 91–93°).

(*vi*) Acetophenone azine (isomer A yellow, m.p. 123–124°).

(*vii*) Benzophenone azine (creamy white, m.p. 166–168°).

Improved salicylaldehyde tests for hydrazine are given below

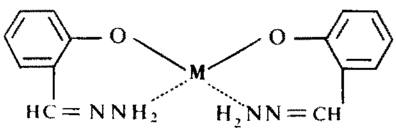
(*i*) Add test solution gradually with stirring to excess of ethanolic solution of salicylaldehyde in a small beaker and heat on a water-bath for at least 30 min. A bright yellow precipitate indicates that hydrazine is present.

Confirmatory tests are as follows.

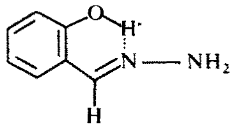
(*ii*) With the test solution in a small beaker, add ethanolic salicylaldehyde solution drop by drop with stirring. If hydrazine is present, a whitish precipitate of salicylaldehyde hydrazone settles after the reaction mixture has cooled. Excess of salicylaldehyde leads to formation of the azine.

(*iii*) Chill both test solution and ethanolic salicylaldehyde solution in an ice–salt bath for at least 30 min and then add the test solution with stirring to the salicylaldehyde (still in the ice–salt bath). If hydrazine is present in the test solution, continued stirring produces a pink solid which is one geometrical isomer of salicylaldehyde azine. For this test to be successful, concentrated solutions of reactants should be used so as to obtain copious precipitates.

As to the Cu(II) chelates of salicylaldehyde hydrazone and salicylaldehyde azine, it is possible that the shiny crystalline leaves (m.p. 98°) prepared by Terentev *et al.*[6] were simply salicylaldehyde hydrazone crystals. The arguments of Jain *et al.*[2] appear valid, and their suggested structure for the complex formed between Cu^{2+} and salicylaldehyde hydrazone is consistent with the following experimental evidence obtained in our laboratories.



(1) The infrared spectrum of salicylaldehyde hydrazone shows $\nu(C = N)$ at 1620 cm^{-1} and $\nu(NH_2)$ (two peaks) at 3283 and 3380 cm^{-1}. The OH-vibration frequency is absent, apparently because of very strong hydrogen-bonding leading to the formation of a heterocyclic six-membered ring:



The greyish-brown solid complex with m.p. > 300° has $\nu(C = N)$ at 1623 cm^{-1} but the $\nu(NH_2)$ peaks have shifted to 3140 and 3280 cm^{-1}, indicating that whereas the nitrogen atom of C = N is not involved in bonding, the *p*-orbital of the nitrogen atom in NH_2 is.

(2) The Cu(II) salicylaldehyde hydrazone complex, $C_{14}H_{14}O_2N_4Cu$, requires C 50.40%, H 4.23% and N 16.79%; the values found are C 50.3%, H 4.2% and N 16.6%.

The yellow isomer of salicylaldehyde azine, on the other hand, forms an orange-brown solid complex (m.p. 228°) with Cu(II). Preliminary infrared studies indicate that C = N is again not involved in the bonding. The only alternative donor sites left in the ligand are the hydroxyl groups, the vibrational frequencies of which are absent in the infrared spectrum. Further studies on this complex are in progress.

REFERENCES

1. F. Feigl, *Spot Tests in Inorganic Analysis*, 5th Ed., p. 239. Elsevier, Amsterdam, 1968.
2. M. P. Jain and S. Kumar, *Talanta*, 1977, **24**, 149.
3. D. J. Cram and G. S. Hammond, *Organic Chemistry*, 2nd Ed., p. 378. McGraw-Hill, New York, 1964.
4. L. N. Ferguson and G. E. K. Branch, *J. Am. Chem. Soc.*, 1944, **66**, 1467.
5. E. C. Okafor, *J. Org. Chem.*, in the press.
6. A. P. Terentev, E. G. Ruchadze and Z. A. Fadeeva, *Zh. Analit. Khim.*, 1952, **7**, 120.