

CONDENSATION OF ALDEHYDES WITH MALONIC ACID. PART XXI.
CONDENSATION OF 5-BROMOVANILLIN. THE INFLUENCE OF
A BROMO GROUP IN ASSOCIATION WITH A HYDROXY
AND A METHOXY GROUP

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5-Bromovanillin is condensed with malonic acid and gives, instead of the expected cinnamic acid derivative, 5-bromo-3-methoxy-4-hydroxybenzylidene-malonic acid. Under special conditions the yield approaches 70%.

Earlier studies have shown that in the aldehyde-malonic acid condensations, in the presence of a trace of pyridine, the hydroxy group in the *ortho* and the *para* positions has on the whole a retarding influence (Kurien, Pandya, and Surange, *J. Indian Chem. Soc.*, 1934, 11, 823; Pandya and Vahidy, *Proc. Ind. Acad. Sci.*, 1936 4A, 140). With a methoxy group, on the other hand, the aldehyde condensed well and gave better yields (Pandya and Vahidy, *ibid.*, 1936, 4A, 134; 1937, 5A, 437). In the case of vanillin, which is 3-methoxy-4-hydroxybenzaldehyde, the yields were better than those obtained with protocatechuic aldehyde (3:4-dihydroxybenzaldehyde) (Pandya and Sodhi, *ibid.*, 1939, 9A, 511). It has also been found that a bromine group assists the reaction and increases the yield (Pandya and Miss Pandya, *ibid.*, 1943, 18A, 164; Gauri Shankar Gupta, Thesis, 1943, unpublished).

Vanillin-malonic acid condensations gave yields in 3½ hours of 51-61%; 5-bromovanillin gave yields rising up to 70% in 8 hours. Under ordinary conditions with 6 hours' heating and a trace of pyridine the yield was smaller, only 38%. The aldehyde melts at 163° and malonic acid decomposes long before that temperature is reached. To obviate this difficulty experiments with increasing amounts of pyridine were made, but the yields did not improve much. It is interesting to note that Perkin's method altogether failed to give any product, while Vorsatz' method of employing more pyridine (6 mols.) and keeping three weeks at room temperature succeeded. Robinson and Shinoda's method (*J. Chem. Soc.*, 1925, 1977) gave a fairly good yield (44%). In absolute alcoholic solution and with pyridine, the yield was 70%.

Another important point is that the product of the reaction is *not* the expected monobasic acid derivative, but is the dibasic malonic acid derivative, showing that here, under the conditions tried, bromine did not allow decarboxylation to occur. This has been found to be usual with heavy-weighted aldehydes (cf. Parts XVIII and XX, *this Journal*, 1947, 24, 437, 447.)

E X P E R I M E N T A L

5-Bromovanillin was prepared according to the method of Dakin (*J. Amer. Chem. Soc.*, 1920, 42, 493). Recrystallised from hot alcohol it melted at 153° (Dakin, m.p. 163-64°), yield 87%.

Condensation in the presence of a Trace of Pyridine.—5-Bromovanillin (1.15 g.), malonic acid (0.5 g.) and pyridine (0.07-0.08 c.c.) (1 : 1 : 0.2 mol.) were heated on a water-bath (98°) for 6 hours. No other change excepting the appearance of a slight yellow colour was noticed. After cooling, the mixture was extracted with ammonium carbonate solution (10%). The original aldehyde is soluble in sodium carbonate solution. About half the product went in solution. After filtration and acidification, a white precipitate was obtained melting at 220°; after several crystallisations from hot alcohol, the melting point became constant at 245° (decomp.). The yield of 5-bromo-3-methoxy-4-hydroxybenzylidene-malonic acid was 38% of theory. (The residue after treatment with alkali was the unreacted aldehyde).

In all the succeeding experiments, the identical product was obtained, as was shown by the mixed melting point and by other properties.

Condensation in the presence of Pyridine (1 mol.).—Aldehyde (1.15 g.), malonic acid (0.5 g.), 0.4 c.c. of pyridine (1 : 1 : 1 mol.) were heated together in the same way (6 hours). Foam and bubbles were observed. On repeating the above treatment, the identical acid in the same yield was obtained.

Condensation without any condensing agent.—(i). No reaction was found to take place after 6 hours' heating on a water-bath.

(ii). In a second experiment the reaction mixture was heated at 115-120° for 8 hours. The mixture had become of a light violet colour. The same acid in a lower yield (31%) was obtained, a great deal of the unused aldehyde was recovered.

Condensation in the presence of Pyridine (3 mols.).—The substances were taken in 1 : 1 : 3 mols. (1.15 g., 0.5 g. and 1.2 c.c.) and were heated on a water-bath for 6 hours. Evolution of a gas was noticed. The same acid in 31% yield was obtained.

Condensation by Perkin's Method.—The aldehyde (1.15 g.), freshly fused sodium acetate (0.5 g.) and acetic anhydride (0.8 c.c.) (1 : 1 : 2 mols.) were heated at 170-180° for 10 hours. The aldehyde was recovered unchanged.

Condensation at room temperature in the presence of Pyridine (7 mols.).—The same amounts of the aldehyde and malonic acid, with 2.8 c.c. of pyridine, were kept for 3 weeks at room temperature (25-35°). A yellow precipitate separating was taken out and therefrom the identical acid was recovered in the usual way but in a smaller yield (19%).

Condensation on a water-bath in the presence of pyridine (5 mols.) gave a 32% yield.

Condensation by Robinson-Shinoda's method (loc. cit.).—Aldehyde (1.15 g.), malonic acid (1.6 g.), pyridine (2.1 c.c.) and piperidine (two drops) were heated on a water-bath (reflux condenser) for 3 hours. The flask was heated on the direct flame (wire gauze) for 15 minutes. A yellowish precipitate came down which after several crystallisations gave the same acid, m. p. 245°, yield 44% of theory.

When the aldehyde and malonic acid were taken with pyridine (1 : 1 : 2) and enough of absolute alcohol, and refluxed for over 8 hours on a water-bath, the yield was over 70%.

The acid obtained was insoluble in cold or hot water, ether, chloroform and benzene; sparingly soluble in cold alcohol, and quite soluble in hot alcohol, acetone and acetic acid.

It decolorised both bromine water and alkaline permanganate, suggesting unsaturation or a reducing (phenolic) group, or both. In alcoholic solution it gave a green colour with ferric chloride, indicating a phenolic group.

Equivalent weight, by titration with sodium hydroxide solution, was 155.4 and 155.6. The unsaturated monobasic acid, 3-methoxy-4-hydroxy-5-bromobenzylidene-acetic acid ($C_{10}H_9O_4Br$) requires 272.9, while the unsaturated dibasic acid, 3-methoxy-4-hydroxy-5-bromobenzylidene-malonic acid ($C_{11}H_9O_6Br$) requires 158.5.

The silver salt method and Rast's method of finding the molecular weight were both inapplicable as the acid decomposed under the conditions of the experiments.

Bromine was estimated by the fusion method with sodium peroxide. [Found: Br, 25.42, 25.66. The mono acid (above) $C_{10}H_9O_4Br$ requires Br, 29.30%, while the dibasic acid (above) $C_{11}H_9O_6Br$ requires Br, 25.24%].

Several of the usual methods for decarboxylating the dibasic malonic acid to the corresponding monobasic acid were tried, but without success. (Compare the corresponding acids from the two nitrosalicylaldehydes: Pandya, Saxena and Tinku, *J. Indian Chem. Soc.*, 1947, 24, 433, 443).

REVIEW

Inorganic Chemistry—By Fritz Ephraim. Translated by P. C. L. Thorne and E. R. Roberts. Published by Gurney and Jackson, London, 1943; pp. 921; price 28sh.

The present volume is the fourth English edition of the well-known German Text, *Anorganische Chemie*, by Fritz Ephraim. Many new materials have been incorporated in the present edition in order to include the latest informations on some topics, relating particularly to valency, radioactivity, isotopes, and a few new compounds and reactions. On the whole, the book undoubtedly represents a marked improvement on its last edition, and will certainly maintain the high reputation which Ephraim's text-book has enjoyed since its first publication nearly a quarter of a century ago. It cannot be too strongly recommended to the teachers and advanced students of Inorganic Chemistry. Few text-books in science have survived such a long period of time without losing its popularity and usefulness, and that even after the death of its author. This, in itself, is an indisputable evidence of its merit. The present edition is very well got up, and the printing and binding leave nothing to be desired. There are, however, a few errors, typographical and factual, that have come to the notice of the reviewer. These are enumerated below so that they might be removed in the next edition of the book.

1. In the preface itself there is a mention of some figures on pp. 123, 755, 842, and 305. In the actual text, however, these pages are absolutely free from all figures.

2. On p. 3, it is written that "the product of the error and the momentum is equal to a constant, Planck's universal constant h ". This is obviously wrong and should be replaced by "the product of the errors in measuring the position and the momentum is equal to a constant etc...".

3. On p.4, line 1, "to calculate the series of lines etc" should be replaced by "to calculate the frequencies of the series etc.."

On the same page in para 2, it is written that "the orbit nearest the nucleus is described as the $\frac{1}{2}K$ -level etc...". No distinction is made between the orbits and levels. This is rather confusing and inaccurate.

Again on the same page, towards the bottom, the spin quantum number, m_s , is defined as the direction of the electron spin in a magnetic field. There is no justification in ascribing the spin of the electron to an external magnetic field.

4. On p. 50, line 13 from the top, it is stated that "the variations of valency are, however, more often due to the fact that some of the compounds are electrovalency compounds and some covalency compounds etc...".

The statement is not a precise one.

5. On p. 55, last line, the bond angle 200° for F_2O should be 100° :

6. On p. 69, line 14 from the top, it is written that "in equal times equal numbers of atoms of the same radio-element are decomposed, which is characteristic of reactions of the first order." This is obviously wrong.

A confusion is made between number and concentration.

7. On p. 70, para 2, it is written that "the term mean life period indicates the number of atoms out of which one is disintegrated per day." This is not a correct and happy statement.

8. On p. 114, line 8 from the top, the word 'atomicity' has been used to mean molecular composition. This is rather unusual.

9. On p. 142, line 8 from the top :—"The low value for the hardness of graphite depends on the fact that in the ordinary test only the fourth and the weakest valency of the carbon atom comes into play, that is parallel to the cleavage plane. At right angles to these planes the hardness approaches that of the diamond".

The fact is, however, quite the contrary.

10. On p. 213, near the bottom, it is stated that Au, Pt and Pd are dissolved from the alloy in nitric acid etc. Obviously, nitric acid should be replaced by aqua regia.

11. On p. 231, line 2, the relative *masses* should be replaced by relative *numbers*; and in line 8, *polarisability* should be replaced by *polarising power*.

12. On p. 235, line 13, cuprous iodide is described as *pale yellow*; but we know it to be *white*.

13. On p. 287, Sugden's formulation of co-ordination compounds with semipolar singlet linkage might have been profitably omitted, as there is no theoretical and experimental justification behind it.

14. On p. 295, in the line below the table, it is stated that "the presence of H^+ ions retards the conversion of the violet into the green form". This has been wrongly translated and should be "..... retards the formation of the violet from the green form".

15. On p. 310, just over the heading *Cobaltamines and Chromamines* it is stated that "the cyanogen in these compounds can also be replaced by other radicals, but these substances have *not been studied* in detail. The translators have here overlooked the description and study of a large number of substituted cyano-cobaltates containing S_2O_3 , SO_3 and H_2O groups. These might have been included as interesting and welcome materials in the present edition.

16. On p. 383, line 1, the words "radii of univalent cations" should be replaced by 'univalent radii of cations'; and in line 3, Be^{3+} should be replaced by Be^{2+} .

17. On p. 556, line 4 from the bottom, CaCl should be replaced by KCl.

18. On p. 556, in line 3 from the bottom, it is written that "sulphides of the ammonium sulphide group are precipitated when the solutions are acidified". This cannot be correct as these sulphides are not precipitated in acid solutions, and with the exception of CoS and NiS they are soluble in acids.

While discussing the constitution of thiosulphates the authors have made no mention of the isomerism of thiosulphuric acid, which is now well known.

19. On p. 599, S_2Cl_2 is described wrongly as *light* yellow, while it should be *dark* yellow.

20. On p. 676 in line 19 and 20, in the formula showing resonance for nitric oxide, the single bonds should be replaced by double bonds.

21. On p. 700, under *Analogy with Chlorates*, it is stated that the chlorates and nitrates are isomorphous; and the entire para is devoted to explain the analogy between the two. It has been stated further that the recent work of Pauling indicates a fundamental similarity in their electronic structure.

All these are incorrect. Chlorates with pyramidal structure (bond angles 106°) cannot be isomorphous with nitrates having planar structure (bond angles 120°), though they may have closely similar properties. It is the carbonate radical which may be isomorphous with the nitrate, as they are isoelectronic and isosteric.

22. On p. 757, in line 4, antimony is stated to be quadrivalent in $M_2[SbX_6]$. Magnetic measurements have, however, shown them to be mixtures of ter- and quinquevalent antimony.

23. On p. 840, in the equation for the formation of hypoborate, $KOBH_3$ should be replaced by $KOBH_2$.

24. On p. 841, the formula for hypoboric acid should $[BOH_2]H$ and not $[BOH_3]H$.

Considering, however, the volume of the book, the number of errors is large, but some of them are of a quite serious type and cannot be ignored.

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