

Wahl and Faivret⁴ obtained a 5-methylisatide by condensing dioxindole with 5-methylisatin. The condensation of 5-methyldioxindole with isatin gives the same 5-methylisatide. This fact precludes acceptance of the quinhydrone formulation and strongly supports the symmetrical isatin pinacol formula.

Experimental

5-Methylisatide. A. From 5-methylisatin and dioxindole, Method of Wahl and Faivret.—Ten drops of piperidine was added to a solution of 1.9 g. of dioxindole and 2 g. of 5-methylisatin in 50 cc. of 95% ethyl alcohol and the whole heated on the water-bath under a reflux condenser for one hour. After cooling the precipitate was filtered off and washed repeatedly with small portions of alcohol. The straw colored powder so obtained could not be crystallized from any of the usual organic solvents. The yield was 3.1 g. or 81% of the theoretical. The substance softened at about 220° and melted with decomposition at 228–230°. Wahl and Faivret reported 229–230°.

B. From Isatin and 5-Methyldioxindole.—The procedure was identical with that described above. The substance softened at about 220° and melted with decomposition at 227–230°. A mixture of this substance with the 5-methylisatide prepared from dioxindole and 5-methylisatin melted with decomposition at 227–230°. The yield was 3 g. or 79% of the theoretical.

The writer is indebted to the Dow Chemical Co. for the gift of a generous supply of indigo from which the isatin and dioxindole used in this work were prepared.

Summary

The condensation of 5-methyldioxindole with isatin yields the same 5-methylisatide obtained by Wahl and Faivret from 5-methylisatin and dioxindole. In the light of this fact the unsymmetrical quinhydrone formulation for isatide is untenable. The isatin pinacol formula is probably correct.

⁴ Wahl and Faivret, *Ann. chim.*, 5, 314 (1926).

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF STANFORD UNIVERSITY]

THE NUMBER OF STRUCTURAL ISOMERS OF CERTAIN HOMOLOGS OF METHANE AND METHANOL

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A very ingenious general method for determining the number of structurally isomeric paraffin hydrocarbons has been published recently.¹ The purpose of this article is to extend the results previously given by applying this method to the computation of the number of structural isomers of hydrocarbons of the methane series of carbon contents ranging from twenty to forty, inclusive, and of hexacontane.

In order to calculate the number of structural isomers of a given paraffin hydrocarbon by the method referred to above, it is first necessary to know

¹ Henze and Blair, *THIS JOURNAL*, 53, 3077 (1931).

the numbers of all structurally isomeric alcohols of the methanol series of carbon content not exceeding one-half that of the hydrocarbon. Table I represents the number of structurally isomeric saturated monohydric alcohols containing from twenty to thirty carbon atoms per molecule, computed according to the method of Henze and Blair,² and augments the values listed by them.

TABLE I
THE NUMBER OF STRUCTURALLY ISOMERIC HOMOLOGS OF METHANOL

| Carbon content | Primary | Secondary | Tertiary | Total |
|----------------|----------------|----------------|----------------|----------------|
| 21 | 5,622,109 | 5,806,256 | 3,287,448 | 14,715,813 |
| 22 | 14,715,813 | 15,256,265 | 8,677,074 | 38,649,152 |
| 23 | 38,649,152 | 40,210,657 | 22,962,118 | 101,821,927 |
| 24 | 101,821,927 | 106,273,050 | 60,915,508 | 269,010,485 |
| 25 | 269,010,485 | 281,593,237 | 161,962,845 | 712,566,567 |
| 26 | 712,566,567 | 747,890,675 | 431,536,102 | 1,891,993,344 |
| 27 | 1,891,993,344 | 1,990,689,459 | 1,152,022,025 | 5,034,704,828 |
| 28 | 5,034,704,828 | 5,309,397,294 | 3,081,015,684 | 13,425,117,806 |
| 29 | 13,425,117,806 | 14,187,485,959 | 8,253,947,104 | 35,866,550,869 |
| 30 | 35,866,550,869 | 37,977,600,390 | 22,147,214,029 | 95,991,365,288 |

The inverse ratios of consecutive numbers in the last column are very nearly constant, but always slightly increasing, and possess ever diminishing first differences. Assuming that the numbers in the last column are in geometric progression, and extrapolating the value of the average common ratio over the carbon content interval from 30 to 35, the number of structurally isomeric alcohols of the formula $C_{35}H_{71}OH$ can be estimated as: $T_{35} = (2.688)^5 T_{30} = 1.35 \times 10^{13}$. Taking the average common ratio over the carbon content interval from 30 to 40 as 2.695, by a similar computation the corresponding value for $C_{40}H_{81}OH$ is 1.94×10^{15} .

Table II contains the number of structurally isomeric hydrocarbons of the methane series, and supplements the results previously found.³ The

TABLE II
THE NUMBER OF STRUCTURALLY ISOMERIC PARAFFINS

| Carbon content | Number of isomers | Carbon content | Number of isomers |
|----------------|-------------------|----------------|--------------------------------|
| 19 | 148,284 | 31 | 10,660,307,791 |
| 21 | 910,726 | 32 | 27,711,252,769 |
| 22 | 2,278,658 | 33 | 72,214,088,660 |
| 23 | 5,731,580 | 34 | 188,626,236,139 |
| 24 | 14,490,245 | 35 | 493,782,952,902 |
| 26 | 93,839,412 | 36 | 1,295,297,588,128 |
| 27 | 240,215,803 | 37 | 3,404,490,780,161 |
| 28 | 617,105,614 | 38 | 8,964,747,474,595 |
| 29 | 1,590,372,121 | 39 | 23,647,478,933,969 |
| | | 60 | 22,158,734,535,770,411,074,184 |

² Henze and Blair, THIS JOURNAL, 53, 3042 (1931).

³ Ref. 2, p. 3084.

number of isomers of $C_{19}H_{40}$ was found to be in error, and the correct value is here given. As in the case of the alcohols, the numbers of structurally isomeric hydrocarbons also form an approximate geometric progression. Here again the inverse ratios of successive numbers are always slightly increasing, and have decreasing first differences. The extrapolated average inverse ratio of consecutive numbers over the carbon content interval from 60 to 70 is 2.72, and hence the value for $C_{70}H_{142}$ is approximately 4.91×10^{26} .

Several corrections are to be noted in the original papers by Henze and Blair. On line 2, p. 3045, for " $(n-1)6$ an integer," read $(n-1)/6$ an integer. In the discussion of the number of hydrocarbons of even carbon content of group A, p. 3080, line 19, the factor $1/2$ should be inserted to make the formula read correctly. This remark also applies to the formula for hydrocarbons of odd carbon content resulting from joining alkyls of $(N+1)/2$ and $(N-1)/2$ carbon atoms through an intermediate carbon atom, p. 3080, line 36. In group B, type b, Case 2, page 3082, line 23, it might be well to mention explicitly that j and k cannot interchange values, which may be expressed by requiring that j always exceed k . For completeness, it may be added that in the formula for compounds of odd carbon content of Group A, it is implied that the definition of T_0 is unity. These corrections apply to the references noted, but were correctly applied in the computations of the authors.

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MOLECULAR REARRANGEMENT IN THE HYDROLYSIS OF CHLOROTOLUENES WITH ALKALI

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It is known that molecular rearrangement takes place when ortho or para chlorobenzene sulfonic acid is fused with potash, both compounds yielding resorcinol by this treatment.¹ It now appears that such a rearrangement may be general with halogen substituted benzenes carrying aliphatic side chains. We have carried out a number of experiments on the hydrolysis of substituted chlorobenzenes carrying normal aliphatic side chains and have been singularly unsuccessful in obtaining pure products. This was particularly apparent in the case of the products obtained from the hydrolysis of ortho and para chloro substituted derivatives of ethylbenzene, normal butylbenzene, and normal amylbenzene. These compounds are not adequately described in the literature and the phenols derived from them have been described² but there are no quantitative methods for purifying

¹ Beilstein, 4th ed., Vol. VI, p. 796.

² Coulthard, Marshall and Pyman, *J. Chem. Soc.*, 280 (1930).