The 2,3,5-trimethoxyphenylacetic acid was prepared from the corresponding 2,3,5-trimethoxybenzaldehyde.

The trimethoxyphenylacetic acid obtained from derritol methyl ether was converted into its ethyl ester, which yielded the diphenylcarbinol by the Grignard reaction. This carbinol was dehydrated to the corresponding trimethoxyphenyldiphenylethylene, which was oxidized to a trimethoxybenzoic acid. This acid proved to be identical with 2,4,5-trimethoxybenzoic acid (asaronic acid).

The same acid was obtained by direct oxidation of derritol methyl ether and derritol itself yielded a dimethoxyhydroxybenzoic acid.

WASHINGTON, D. C.

THE NUMBER OF ISOMERIC HYDROCARBONS OF THE METHANE SERIES

By Henry R. Henze and Charles M. Blair

At various times attempts have been made by both mathematicians and chemists to derive a formula by which the number of isomeric hydrocarbons of the methane series could be calculated.

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Apparently the first attempt to derive such a formula was made by the English mathematician Cayley[1] in 1875. He recognized that the number of isomers for a given carbon content was dependent upon the number of those of lesser carbon contents, and thus he obtained successively for every magnitude an expression for the fundamental chains common to all of magnitude N. This function led to the building of "centric and bicentric trees," and with the help of the same he predicted the number of isomeric hydrocarbons inclusive of a carbon content of thirteen. However, his predictions of the number of isomers for the carbon contents of twelve and thirteen were in error.

Almost simultaneously with this attempt of Cayley was that of Schiff.[2] Using a method involving combinations and permutations, he calculated the number of isomeric hydrocarbons through the dodecanes, obtaining for the dodecanes, however, the same erroneous value as that of Cayley.

This error, along with that of Cayley as to the number of tridecanes, was first corrected by Hermann[3] about five years later. The latter divided the structural formulas of the isomers into types, according to the number of branches attached to the fundamental chain of each, and attempted to relate the number of isomers of each type to the total number

[1] Cayley, Ber., 8, 1056 (1875).

[2] Schiff, ibid., 8, 1542 (1875).

[3] Hermann, ibid., 13, 792 (1880); 30, 2423 (1897); 31, 91 (1898).

Hermann

of hydrocarbons. His results were limited to the series CH_4–$C_{13}H_{28}$ and the utilization of his method of calculation does not allow one to predict accurately the number of isomers of the hydrocarbons more complex than the tridecanes.

In 1893, Tiemann[4] also recognized the existence of various types of isomers (monomethyl, dimethyl, monoethyl, etc.), and using an abbreviated numerical system of writing these isomers, counted their number. He recorded the results inclusive of the decanes, but his totals for the nonanes and decanes were incorrect.

This problem of calculating the number of isomeric hydrocarbons was attacked by Delannoy[5] at about the same time but from an entirely different angle. He developed an empirical formula in which an additional term was brought into use with each unit increase in the carbon content. This formula served to calculate the number of isomers through the tridecanes, but it does not hold for those of higher carbon contents.

Another effort at solution of this problem by use of combinations, permutations and variations was that of Losanitsch,[6] who attempted to apply these in determining the number of isomers of each of the types into which he divided the hydrocarbons. He tabulated the number of isomers of certain types through $C_{20}H_{42}$ but summed these so as to obtain the total number of isomers only inclusive of $C_{14}H_{30}$. It is to be noted that his results for $C_{12}H_{26}$ and $C_{14}H_{30}$ are in error.

Goldberg,[7] in 1898, observing that the previously advanced formulas were complicated and difficult to apply, attempted to derive a simpler formula for calculating the number of hydrocarbons. He developed such a formula but, unfortunately, it did not hold above $C_{10}H_{22}$, the totals calculated becoming increasingly below the actual number of isomers. Goldberg recognized this drawback, and, desiring to obtain the number of isomers for higher carbon contents, adopted the Geneva system to number the branch chains and wrote, in an abbreviated form, the structural formulas of all isomers inclusive of the undecanes, but made no predictions for any higher homologs.

For the period of twenty-five years following the work of Goldberg no further reference to this problem is to be found recorded in the literature. The next work appearing is that of Trautz,[8] who in 1924 published a rigorous mathematical treatment of this question. However, this work, combinatorial in nature, was centered upon the substituted hydrocarbons rather than upon the paraffins themselves and cannot be used inaccurately predicting the number of isomers except for those of low carbon content.

4 Tiemann, *Ber.*, 26, 1605 (1893).
5 Delannoy, *Bull. soc. chim.*, [3] 11, 239 (1894).
6 Losanitsch, *Ber.*, 30, 1917, 3059 (1897).
7 Goldberg, *Chem.-Ztg.*, 22, 395 (1898).
8 Trautz, "Lehrbuch der Chemie," Berlin, 1924, Vol. III, p. 23.

The most recent attempt recorded in literature is that of David[9] in 1928. His formula is only a slight modification of that of Delannoy, in which an additional term was added for each unit increase in carbon content, and is of no value in calculating the number of isomers for carbon contents greater than eleven.

It is seen, therefore, that the mathematical formulas which have been advanced for calculating the number of isomeric hydrocarbons, when tested by actual writing and counting of the structural formulas, are found to be correct only inclusive of that carbon content for which they were derived and are in error in predicting the number of isomers for higher carbon contents. The cause for these errors is readily seen, for a formula based upon a "centric" or a "bicentric" center of symmetry will obviously become in error when the carbon content increases so that additional centers of symmetry are introduced. Similarly, formulas so derived that an additional term must be added for each unit increase in the carbon content will also be in error for all carbon contents greater than that for which the additional terms can be definitely established.

It seemed desirable, therefore, to derive a formula which would accurately estimate the number of isomeric hydrocarbons. Attempts to derive such a formula soon showed that no simple mathematical relationship exists between the total number of isomers and their carbon content. The problem was solved only by establishing a relationship between the number of isomeric hydrocarbons of a given carbon content and the previously calculated number of isomeric alcohols of lesser carbon contents. This relationship is in direct contrast to the idea held by previous workers who considered the number of alcohols to be conditioned by the number of hydrocarbons from which, theoretically, the former might be derived.

Theoretical Discussion

In this treatment we find it desirable to separate the hydrocarbons into classes according to whether their carbon content is even or odd. Those hydrocarbons whose carbon content, N, is an even number, are further divided into two groups: A, consisting of those hydrocarbons whose graphic formula may be divided into two parts of $N/2$ carbon atoms each; and B, the remaining isomeric hydrocarbons whose graphic formula cannot be so divided. Division of the graphic formula into two parts signifies breaking the single bond between two adjacent carbon atoms, thus obtaining two alkyl radicals.

Likewise, the hydrocarbons whose carbon content, N, is an odd number, are also divided into two groups: A, consisting of those hydrocarbons whose graphic formula can be divided into two parts, one of $(N + 1)/2$ carbon atoms and the other of $(N - 1)/2$ carbon atoms; and B, con-

9 David, *Rev. gén. sci.*, 39, 142 (1928).

sisting of the remaining hydrocarbons whose graphic formula cannot be so divided.

For the hydrocarbons of even carbon content, in calculating the number of isomers in group A, two factors are utilized: (I), the number of possible alkyl radicals of $N/2$ carbon atoms, and (II), the number of possibilities, without exception or repetition, of combining the alkyl radicals of $N/2$ carbon atoms with those of $N/2$ carbon atoms.

(I). The number of paraffin alkyl radicals of a given carbon content is equal to the number of isomeric alcohols of that carbon content. The method of calculating this number has been previously determined.[10]

(II). If two alkyl radicals of $N/2$ carbon atoms each are combined, a hydrocarbon of N carbon atoms is obtained. Therefore, the number of hydrocarbons of N carbon atoms that may be obtained will depend upon the number of alkyl radicals of $N/2$ carbon atoms; and, since each isomeric alkyl radical is a distinct substance, the number of combinations of the $T_{N/2}$ alkyl radicals of $N/2$ carbon atoms, taken one at a time, with the $T_{N/2}$ alkyl radicals of $N/2$ carbon atoms, taken one at a time, may be calculated by the mathematical formula for this type of combination, that is

$$T_{N/2}(1 + T_{N/2})$$

For the hydrocarbons of odd carbon content, in calculating the number of isomers in group A, two factors are also utilized: (I), the number of possible alkyl radicals of $(N + 1)/2$ carbon atoms and of $(N - 1)/2$ carbon atoms, and (II), the number of possibilities, without exception or repetition, of combining the alkyl radicals of $(N + 1)/2$ carbon atoms, taken one at a time, with those of $(N - 1)/2$ carbon atoms, also taken one at a time. In order to prevent duplication in determining the number of these combinations, it is necessary to recognize that part of the alkyl radicals of $(N + 1)/2$ carbon atoms may be derived from the alkyl radicals of $(N - 1)/2$ carbon atoms by the addition to the free valence of the latter, of the —CH_2— group. Hence, the hydrocarbons resulting from combining such portion of the alkyls of $(N + 1)/2$ carbon atoms, that may be so derived, with the alkyls of $(N - 1)/2$ carbon atoms are considered as being formed by joining the alkyls of $(N - 1)/2$ carbon atoms to the alkyls of $(N - 1)/2$ carbon atoms through an intermediate carbon atom, and the number of such possible combinations will equal $T_{(N - 1)/2}(1 + T_{(N - 1)/2})$, where T is the total number of alcohols of all types containing the number of carbon atoms represented by its subscript. The combination of the remaining portion of the alkyls of $(N + 1)/2$ carbon atoms with the alkyls of $(N - 1)/2$ carbon atoms will form the balance of the isomeric hydrocarbons of group A, and the calculation of their number will be made by the mathematical formula

$$T_{(N - 1)/2}(T_{(N + 1)/2} - T_{(N - 1)/2})$$

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

The total number of hydrocarbons in group A will consist, therefore, of the sum of the number of hydrocarbons obtained in these two ways. Hence, the number of isomers in group A will equal

$$\frac{T_{(N-1)/2}(1 + 2T_{(N+1)/2} - T_{(N-1)/2})}{2}$$

If the graphic formula of the hydrocarbons of even carbon content cannot be divided into two parts of $N/2$ carbon atoms each there must be in the formula one carbon atom, and only one, to which are attached branches none of which may contain more than $(N/2 - 1)$ carbon atoms. Obviously, there must be at least three branches, and since carbon has only four valences, there cannot be more than four branches.

Similarly, for those hydrocarbons of odd carbon content whose graphic formulas cannot be divided into two parts, one of $(N + 1)/2$ carbon atoms and the other of $(N - 1)/2$ carbon atoms, there must be in each of such formulas one carbon atom, and only one, to which are attached branches none of which may contain more than $(N - 3)/2$ carbon atoms. By a treatment similar to that already utilized in the case of the hydrocarbons of even carbon content, it may be shown that this specified carbon atom must have attached to it either three or four branches.

Hence, the isomeric hydrocarbons of group B, both even and odd, will be of two types: (a), those in which three branches are attached to the specified carbon atom, and (b), those in which four branches are attached to the specified carbon atom. The total number of isomers of group B will be obtained by a summation of types (a) and (b).

Type (a) would seem to consist of three possible cases: (1), in which all three branches were of different carbon content; (2), in which two branches were of the same carbon content and different from the third; (3), in which all three branches were of the same carbon content. All three of these cases are actually possible but all will not necessarily be present with every value of N. The number of isomers in each case may be calculated by the following mathematical formula for that particular case.

Case (1) $\Sigma T_i \cdot T_j \cdot T_k$ (a₁)

where $i + j + k = N - 1$; i, j and k are integers, distinct, and greater than zero; $i > j > k$; i, for even carbon content, is never greater than $(N/2 - 1)$; i, for odd carbon content, is never greater than $(N - 3)/2$.

Case (2) $\frac{1}{2}\Sigma T_i \cdot T_j (1 + T_i)$ (a₂)

where $2i + j = N - 1$; i and j are integers, distinct, and greater than zero; for even carbon content, neither i nor j may be greater than $(N/2 - 1)$; for odd carbon content, neither i nor j may be greater than $(N - 3)/2$.

Case (3) $\frac{1}{6}T_i (1 + T_i)(2 + T_i)$ (a₃)

where $3i = N - 1$; i is an integer greater than zero.

Type (b) would seem to consist of five possible cases: (1), in which all

four branches are of different carbon content; (2), in which two branches are of the same carbon content and each of the others of different content; (3), in which three branches are of the same carbon content and different from the fourth; (4), in which all four branches are of the same carbon content; (5), in which the four branches can be divided into two sets of two branches each, the individual members of each set being of the same carbon content but differing in content from the members of the other set. It will be seen that cases (4) and (5), though theoretically possible for hydrocarbons of both even and odd carbon content, are actually possible only for the latter, for in case (4) $(N - 1)$ should be divisible by four, and in case (5) $(N - 1)$ should be divisible by two. The number of isomers in each case may be calculated by the following mathematical formula for that particular case.

Case (1)
$$\Sigma T_h \cdot T_i \cdot T_j \cdot T_k \qquad (b_1)$$
where $h + i + j + k = N - 1$; h, i, j and k are integers, distinct, and greater than zero; $h > i > j > k$; h, for even carbon content, is never greater than $(N/2 - 1)$; h, for odd carbon content, is never greater than $(N - 3)/2$.

Case (2)
$$\tfrac{1}{2}\Sigma T_i \cdot T_j \cdot T_k (1 + T_i) \qquad (b_2)$$
where $2i + j + k = N - 1$; i, j and k are integers, distinct, and greater than zero.

Case (3)
$$\tfrac{1}{6}\Sigma T_i \cdot T_j (1 + T_i)(2 + T_i) \qquad (b_3)$$
where $3i + j = N - 1$; i and j are integers, distinct, and greater than zero.

Case (4)
$$\tfrac{1}{24} T_i (1 + T_i)(2 + T_i)(3 + T_i) \qquad (b_4)$$
where $4i = N - 1$; i is an integer greater than zero.

Case (5)
$$\tfrac{1}{2}\Sigma T_i \cdot T_j (1 + T_i)(1 + T_j) \qquad (b_5)$$
where $2i + 2j = N - 1$; i and j are integers, distinct, and greater than zero; $i > j$.

The total number of hydrocarbons of N carbon atoms may be determined by adding to the number of isomers calculated in group A the summation of the number calculated in each of the cases of group B.

The actual meaning and use of these recursion type formulas[11] may be illustrated in the calculation of the number of isomeric tetradecanes.[12]

Sample Calculation

Group A. $N = 14$; $N/2 = 7$
$$T_7 \cdot (1 + T_7)/2 = 39 \cdot (1 + 39)/2 = 780$$

[12] The number of isomeric tetradecanes, erroneously calculated as being 1855, first by Losanitsch and later by Trautz, has been accepted without further substantiation and appears in certain recent textbooks of organic chemistry.

Group B. $N-1 = 13$; $N/2-1 = 6$

Type (a)

Case (1)

$T_6 \cdot T_5 \cdot T_2 = 17 \cdot 8 \cdot 1 = 136$
$T_6 \cdot T_4 \cdot T_3 = 17 \cdot 4 \cdot 2 = 136$

Case (2)

$T_6 \cdot T_1 \cdot (1 + T_6)/2 = 17 \cdot 1 \cdot (1 + 17)/2 = 153$
$T_5 \cdot T_3 \cdot (1 + T_5)/2 = 8 \cdot 2 \cdot (1 + 8)/2 = 72$
$T_4 \cdot T_6 \cdot (1 + T_4)/2 = 4 \cdot 8 \cdot (1 + 4)/2 = 80$

Case (3)

This case is not actually possible for this carbon content

Type (b)

Case (1)

$T_6 \cdot T_4 \cdot T_2 \cdot T_1 = 17 \cdot 4 \cdot 1 \cdot 1 = 68$
$T_6 \cdot T_4 \cdot T_3 \cdot T_1 = 8 \cdot 4 \cdot 2 \cdot 1 = 64$

Case (2)

$T_6 \cdot T_2 \cdot T_1 \cdot (1 + T_5)/2 = 8 \cdot 1 \cdot 1 \cdot (1 + 8)/2 = 36$
$T_4 \cdot T_3 \cdot T_2 \cdot (1 + T_4)/2 = 4 \cdot 2 \cdot 1 \cdot (1 + 4)/2 = 20$
$T_3 \cdot T_6 \cdot T_1 \cdot (1 + T_3)/2 = 2 \cdot 17 \cdot 1 \cdot (1 + 2)/2 = 51$
$T_3 \cdot T_5 \cdot T_2 \cdot (1 + T_3)/2 = 2 \cdot 8 \cdot 1 \cdot (1 + 2)/2 = 24$
$T_3 \cdot T_6 \cdot T_3 \cdot (1 + T_2)/2 = 1 \cdot 17 \cdot 2 \cdot (1 + 1)/2 = 34$
$T_2 \cdot T_5 \cdot T_4 \cdot (1 + T_2)/2 = 1 \cdot 8 \cdot 4 \cdot (1 + 1)/2 = 32$
$T_1 \cdot T_6 \cdot T_6 \cdot (1 + T_1)/2 = 1 \cdot 17 \cdot 8 \cdot (1 + 1)/2 = 136$

Case (3)

$T_4 \cdot T_1 \cdot (1 + T_4)(2 + T_4)/6 = 4 \cdot 1 \cdot (1 + 4)(2 + 4)/6 = 20$
$T_3 \cdot T_4 \cdot (1 + T_3)(2 + T_3)/6 = 2 \cdot 4 \cdot (1 + 2)(2 + 2)/6 = 16$

Thus, the number of isomeric tetradecanes equals 1858.

In Table I is to be found a summary of the number of terms actually present in all theoretically possible cases of types (a) and (b) through a carbon content of forty. Since the number of alkyl groups (i. e., the total number of isomeric alcohols) through C_{20} is recorded in a previous contribution, it is now possible to calculate the number of isomeric hydrocarbons of double this carbon content. Hence, to calculate the total number of isomeric hydrocarbons of the methane series of higher carbon content it would become necessary to make a preliminary calculation of the total number of isomeric alcohols of the methanol series of $N/2$ and lesser carbon contents.

The number of isomeric paraffins, as calculated by the use of these recursion type formulas, for certain selected carbon contents is shown in Table II. It should be noted that the data utilized in deriving these recursion formulas were the totals of the isomers of the series C_4H_{10} to $C_{10}H_{22}$ inclusive as obtained by actual writing of their structural formulas. Since the total number of isomeric tridecanes and tetradecanes, as calculated by

TABLE I

NUMBER OF TERMS IN ALL THEORETICALLY POSSIBLE CASES OF (A) AND (B)

Carbon content	1	3	5	7	9	11	13	15	17	19	21	23	25	27	29	31	33	35	37	39
a_1	.	.	.	.	.	.	1	1	2	3	4	5	7	8	10	12	14	16	19	21
a_2	.	.	.	.	1	2	1	3	3	3	4	5	4	6	6	6	7	8	7	9
a_3	.	.	.	1	.	.	1	.	.	1	.	.	1	.	.	1	.	.	1	.
b_1	.	.	.	.	.	1	1	3	5	8	12	18	24	33	43	55	69	86	104	126
b_2	.	.	.	.	1	.	4	4	7	10	14	16	23	26	32	38	45	50	60	66
b_3	.	.	.	.	.	2	.	2	2	2	2	4	2	4	4	4	4	6	4	6
b_4	.	.	1	.	1	.	1	.	1	.	1	.	1	.	1	.	1	.	1	.
b_5	.	.	.	1	1	2	2	3	3	4	4	5	5	6	6	7	7	8	8	9
Total	.	.	1	2	4	7	11	16	23	31	41	53	67	83	102	123	147	174	204	237

Carbon content	2	4	6	8	10	12	14	16	18	20	22	24	26	28	30	32	34	36	38	40
a_1	.	.	.	.	1	1	2	3	4	5	7	8	10	12	14	16	19	21	24	27
a_2	.	.	1	2	1	3	3	3	4	5	4	6	6	6	7	8	7	9	9	9
a_3	.	1	.	.	1	.	.	1	.	.	1	.	.	1	.	.	1	.	.	1
b_1	.	.	.	.	.	1	2	4	7	11	16	23	31	41	53	67	83	102	123	147
b_2	.	.	.	1	3	4	7	10	13	17	22	26	32	38	44	51	59	66	75	84
b_3	.	.	1	1	1	2	2	2	3	3	3	4	4	4	5	5	5	6	6	6
Total	.	1	2	4	7	11	16	23	31	41	53	67	83	102	123	147	174	204	237	274

the recursion formulas, differed from the totals previously accepted in the literature, it seemed desirable also to write and count all the structural formulas, as required by theory, of the undecanes, dodecanes, tridecanes and tetradecanes. The numbers so obtained agree exactly with the totals as calculated by the use of the mathematical formulas.

TABLE II

NUMBER OF ISOMERIC HYDROCARBONS OF THE METHANE SERIES

Carbon content	Number of isomers	Carbon content	Number of isomers
1	1	11	159
2	1	12	355
3	1	13	802
4	2	14	1858
5	3	15	4347
6	5	16	10,359
7	9	17	24,894
8	18	18	60,523
9	35	19	148,284
10	75	20	366,319

Carbon content	Number of isomers
25	36,797,588
30	4,111,846,763
40	62,491,178,805,831

Summary

1. No direct or simple relationship appears to exist between the total number of isomeric hydrocarbons of the methane series and their carbon content.

2. By means of a separation of the isomeric hydrocarbons of each specified carbon content into types, arbitrarily chosen upon the basis of their structural formulas, a relationship may be established between the number of hydrocarbons and the alkyl groups of which the former may be considered to be composed. Mathematical formulas of the (finite) recursion type are advanced which permit of the calculation, from their carbon content, of the number of isomeric hydrocarbons in each of these structural types. In using these recursion formulas to calculate the total number of such hydrocarbons of any given carbon content, the total number of alkyl groups (*i. e.*, the total number of isomeric alcohols) of $N/2$ and all lesser carbon contents must be known.

3. The totals obtained by use of these mathematical formulas agree exactly through the tetradecanes with the numbers required by theory as tested by actually writing all the possible structural formulas.

AUSTIN, TEXAS

THE INFLUENCE OF THE ARSONO GROUP ON THE ACTIVITY OF NUCLEAR CHLORINE

BY R. E. ETZELMILLER[1] AND CLIFF S. HAMILTON

It has long been known that halogens in the benzene nucleus can neither be removed nor replaced by the ordinary reagents which act upon them in the aliphatic series. Nevertheless, the presence of certain groups such as nitro, cyano, carboxyl, etc., loosens the attachment and promotes substitution. Most of the experimental work in the study of replacement reactions has been done with halogeno-nitro compounds. However, as early as 1892, Heidenreich and Victor Meyer[2] showed that *o*-bromobenzoic acid and ammonia reacted at 200° to give diphenylamine. Later, Ullmann[3] made a study of the condensation of *o*-chlorobenzoic acid with aniline and found that a catalyst was necessary, the salts of copper being most effective. The addition of potassium carbonate and the use of nitrobenzene as a solvent were also found to increase the yields.

Since the arsono group is similar in structure to the nitro, carboxyl, and sulfonic acid groups, and is meta directing, halogen in the ortho

[1] Parke, Davis and Company Fellow.
[2] Heidenreich and Meyer, *Ber.*, **25**, 2188 (1892).
[3] Ullmann, *Ann.*, **355**, 312 (1907).