potassium bicarbonate solution and with water, dried over sodium sulfate, and the solvent evaporated. The residue was taken up in acetone, petroleum ether was added and the solution allowed to stand. Crystals of triphenylcarbinol (from the hydrolysis of triphenylmethyl bromide) soon appeared and were filtered off. The α-monopalmitin crystallized out after evaporating part of the solvent and cooling.

Molecular weights were determined for all of the new compounds and most of the intermediates used in their preparation, using the method of Menzies and Wright.[10] with ethyl acetate as the solvent.

Summary

The β-mono-(p-nitrobenzoate) and the α,β-dibenzoate of glycerol have been prepared from glycerol trityl ethers and found to correspond to the compounds previously prepared by Helferich and Sieber. These compounds, when thus prepared, apparently do not undergo a rearrangement involving the migration of the aromatic acyl group. The same procedures when used for the preparation of β-monopalmitin, β-monostearin, α,β-dipalmitin and α,β-distearin resulted in the migration of the aliphatic acyl groups and the production of the isomeric α-monoglycerides and α,α'-diglycerides.

The synthesis and identification of the following compounds has been described: the α,α'-ditrityl ether of β-monostearin, the α,α'-ditrityl ether of β-monolaurin, the α-monotrityl ether of α,β-dipalmitin, the α-monotrityl ether of α,β-distearin, and the α-monotrityl ether of acetoneglycerol.

(10) Menzies and Wright. THIS JOURNAL. 43, 2314 (1921).

PITTSBURGH, PENNSYLVANIA

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TEXAS]

The Number of Structurally Isomeric Hydrocarbons of the Ethylene Series[1]

BY HENRY R. HENZE AND CHARLES M. BLAIR

The method for calculating the number of structural isomers by establishing a unique relationship between the number of structurally isomeric hydrocarbons of the methane series and of the acetylene series and the alkyl groups of which these may be considered to be composed may also be utilized successfully in calculating the number of structurally isomeric hydrocarbons of the ethylene series.

The homologs of ethylene are divided into four groups: A, consisting of those hydrocarbons which may be formed, theoretically, by replacing one hydrogen atom of ethylene by an alkyl radical; B, in which two hydrogen atoms are replaced by alkyl groups; C, in which three hydrogen atoms are replaced by alkyls; and D, in which all four hydrogen atoms are replaced.

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[1] This paper was presented before the Central Texas Section of the American Chemical Society at its annual meeting in Waco, Texas, on April 23, 1932. Previous contributions in this series are Henze and Blair, THIS JOURNAL, 53, 3042-3046, 3077-3085 (1931); 54, 1098-1106, 1538-1545 (1932); Coffman, Blair with Henze, *ibid.*, 55, 252-253 (1933).

Group A.—The total number of structural formulas of olefin hydrocarbons of N carbon atom content included in Group A, $CH_2{=}CHR$, and formed by replacing one hydrogen atom in ethylene by an alkyl radical of $N - 2$ carbon atom content, will equal the total number of such alkyl radicals[2] or $T_{(N-2)}$.

$$A_N = T_{(N-2)} \tag{A}$$

Group B.—The structural formulas of the hydrocarbons of Group B are theoretically of two types: (1), those in which the alkyl radicals, R- and R′- (the carbon content of R- plus R′- always equaling $N-2$), are of unequal carbon content; and (2), in which the alkyls are of equal carbon content. Type (2) is actually impossible with hydrocarbons of uneven carbon content for in this type $N-2$ should be divisible by two. Each of the types (1) and (2) may be further divided into two subtypes: (a), in which the two alkyl radicals are attached to the same carbon atom of the ethylene group, $H_2C{=}CRR'$; and (b), in which the alkyls are not attached to the same carbon atom, $RHC{=}CHR'$. Derivation of (finite) recursion formulas for calculating the number of isomeric hydrocarbons of odd carbon atom content included, respectively, in subtypes (a) and (b) leads to identical expressions. Hence twice the number calculated by means of that formula equals the total number of isomeric homologs of ethylene included in Group B. An analogous relationship exists between subtypes (a) and (b) of the hydrocarbons of even carbon atom content. The following represent such formulas for odd and even carbon atom contents, respectively

Odd:

$$B_N = 2[T_1 \cdot T_{(N-3)} + T_2 \cdot T_{(N-4)} + \ldots T_{(N-3)/2} \cdot T_{(N-1)/2}] \tag{B$_o$}$$

Even:

$$B_N = 2\left[T_1 \cdot T_{(N-3)} + T_2 \cdot T_{(N-4)} + \ldots T_{(N-4)/2} \cdot T_{N/2} + \frac{T_{(N-2)/2} \cdot (1 + T_{(N-2)/2})}{2}\right] \tag{B$_e$}$$

Note that the subscripts in each term add up to $N-2$, and that the number of terms is $(N-3)/2$ for odd carbon content and $(N-2)/2$ for even.

Group C.—The structural formulas of the hydrocarbons included in Group C are theoretically of three types: (1), those in which the alkyl radicals, R-, R′- and R″- (the carbon content of R- plus R′- plus R″- always equaling $N-2$), are of different carbon content; (2), those in which two of the alkyl radicals, R- and R′- are of equal carbon content and different from that of the third, R″-; and (3), those in which all three alkyls are of the same carbon content. Type (3) is actually possible only when $(N-2)/3$ is an integer.

Type (1) may be further divided into three subtypes: (a), in which the alkyl radicals R- and R′- are attached to the same carbon atom of the ethylene group, $RR'C{=}CHR''$; (b), in which R- and R″- are attached

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[2] For the total number of alkyl radicals, which are, of course, numerically equal to the number of structurally isomeric alcohols of the methanol series, through C_{20} see THIS JOURNAL, **53**, 3045 (1931).

to the same carbon atom, RR″C═CHR′; and (c), in which R′- and R″- are attached to the same carbon atom, R′R″C═CHR. Derivation of (finite) recursion formulas for calculating the number of isomeric hydrocarbons included in subtypes (a), (b) and (c) leads to identical expressions. Hence the total number of isomers included in type (1) will equal three times the number calculated by that expression for each subtype or

$$3\Sigma T_i \cdot T_j \cdot T_k \qquad (C_1)$$

where i, j and k are integers, distinct, and greater than zero; $i + j + k = N - 2$; $i > j > k$.

Type (2) may be further divided into two subtypes: (a), in which the two alkyl radicals of equal carbon content are attached to the same carbon atom of the ethylene group, RRC═CHR′; and (b), in which the two alkyls of equal carbon content are not attached to the same carbon atom, RR′C═CHR. The number of isomers included in subtype (a) equals $1/2\Sigma T_i \cdot T_j \cdot (1 + T_i)$. The number of isomers in subtype (b) equals $\Sigma(T_i)^2 \cdot T_j$. Hence, the total number of isomeric homologs of ethylene included in type (2) may be calculated by use of a summation of these two expressions, or

$$1/2\Sigma T_i \cdot T_j \cdot (1 + 3T_i) \qquad (C_2)$$

where i and j are integers, distinct, and greater than zero, and $2i + j = N - 2$.

The total number of isomers of type (3) is given by the expression

$$1/2\Sigma (T_i)^2 \cdot (1 + T_i) \qquad (C_3)$$

where i is an integer greater than zero, and $3i = N - 2$.

Group D.—The structural formulas of the hydrocarbons included in group D are theoretically of five types: (1), those in which the four alkyls R-, R′-, R″- and R‴- are of different carbon content; (2), those in which two of the alkyl radicals are of equal carbon content and each of the others, R′- and R″-, of different carbon content; (3), those in which three of the alkyl radicals are of the same carbon content and different from that of the fourth, R′-; (4), those in which all four alkyls are of the same carbon content; and (5), those in which the four alkyl radicals can be divided into two sets of two each, the individual members of each set being of the same carbon content but differing in carbon content from the members of the other set. It will be seen that types (4) and (5), though theoretically possible for hydrocarbons of both odd and even carbon content, are actually possible only for the latter, for in type (4) $N-2$ should be divisible by four, and in type (5) $N-2$ should be divisible by two.

Type (1) may be further divided into three subtypes: (a), in which the alkyl radicals R- and R′- are attached to the same carbon atom of the ethylene group, RR′C═CR″R‴; (b), in which R- and R″- are attached to the same carbon atom, RR″C═CR′R‴; and (c), in which R- and R‴- are attached to the same carbon atom, RR‴C═CR′R″. Here, again, the expression for the number of isomers in subtype (a) is identical with that for (b) and for (c), hence the total number of isomeric homologs of ethylene of type (1) is given by the formula

$$3\Sigma T_h\cdot T_i\cdot T_j\cdot T_k \qquad (\mathrm{D}_1)$$

where h, i, j and k are integers, distinct, and greater than zero; $h + i + j + k = N - 2$; and $h > i > j > k$.

Type (2) may be further divided into two subtypes: (a), in which the two alkyl radicals of equal carbon content are attached to the same carbon atom of the ethylene group, RRC═CR′R″; and (b), in which the two alkyl radicals of equal carbon content are not attached to the same carbon atom, RR′C═CR″R. The number of isomers included in subtype (a) equals $1/2\Sigma T_i\cdot T_j\cdot T_k\cdot(1 + T_i)$. The number of isomers in subtype (b) equals $\Sigma(T_i)^2\cdot T_j\cdot T_k$. Hence, the total number of isomeric homologs of ethylene included in type (2) is equal to the sum of these expressions, or

$$1/2\Sigma T_i\cdot T_j\cdot T_k\cdot(1 + 3T_i) \qquad (\mathrm{D}_2)$$

where i, j and k are integers, distinct, and greater than zero; $2i + j + k = N - 2$; and $j > k$.

The total number of isomers of type (3) is given by the expression

$$1/2\Sigma(T_i)^2\cdot T_j\cdot(1 + T_i) \qquad (\mathrm{D}_3)$$

where i and j are integers, distinct, and greater than zero; and $3i + j = N - 2$.

The number of isomers of type (4) may be calculated by use of the formula

$$1/8\,[T_i\cdot(1 + T_i)][2 + T_i\cdot(1 + T_i)] \qquad (\mathrm{D}_4)$$

where i is an integer greater than zero, and $4i = N - 2$.

Type (5) may be further divided into two subtypes: (a), in which the two alkyl radicals of equal carbon content are attached to the same carbon atom, RRC═CR′R′, and (b), in which the two alkyl radicals of equal carbon content are not so attached, RR′C═CR′R. The total number of homologs of ethylene of type (5), including both subtypes (a) and (b), may be calculated by the following (finite) recursion formula

$$1/4\Sigma T_i\cdot T_j\cdot(3T_i\cdot T_j + 3 + T_i + T_j) \qquad (\mathrm{D}_5)$$

where i and j are integers, distinct, and greater than zero; $2i + 2j = N - 2$; $i > j$.

In Table I is to be found a summary of the number of terms actually present in all theoretically possible cases of Groups A, B, C and D through a carbon content of forty. Since the number of alkyl groups through C_{20} is recorded in a previous contribution, it is now possible to calculate the number of structurally isomeric hydrocarbons of the ethylene series through a carbon content of twenty-two. Hence, to calculate the total number of structurally isomeric hydrocarbons of this series of higher carbon content it would be necessary to make a preliminary calculation of the total number of alkyl radicals (structurally isomeric monosubstitution products of the paraffins) of $N-2$ and all lesser carbon contents.

TABLE I

NUMBER OF TERMS IN ALL THEORETICALLY POSSIBLE CASES

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	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
B		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
C_1				1	2	4	7	10	14	19	24	30	37	44	52	61	70	80	91	102
C_2			1	1	3	4	4	6	7	7	9	10	10	12	13	13	15	16	16	18
C_3				1			1			1			1			1			1	
D_1						1	2	5	9	15	23	34	47	64	84	108	136	169	206	249
D_2					2	3	8	11	17	23	31	38	49	58	70	82	96	109	126	141
D_3				1	1	3	2	4	4	5	5	7	6	8	8	9	9	11	10	12
D_4			1		1		1		1		1		1		1		1		1	
D_5				1	1	2	2	3	3	4	4	5	5	6	6	7	7	8	8	9
Total	1	2	5	9	15	23	34	47	64	84	108	136	169	206	249	297	351	411	478	551

Carbon content	3	5	7	9	11	13	15	17	19	21	23	25	27	29	31	33	35	37	39	41
A	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
B		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
C_1				1	3	5	8	12	16	21	27	33	40	48	56	65	75	85	96	108
C_2			2	3	3	5	6	6	8	9	9	11	12	12	14	15	15	17	18	18
C_3		1			1			1			1			1			1			1
D_1						1	3	6	11	18	27	39	54	72	94	120	150	185	225	270
D_2				1	4	7	11	17	23	30	39	48	58	70	82	95	110	125	141	159
D_3			1	2	2	3	4	4	5	6	6	7	8	8	9	10	10	11	12	12
Total	1	3	6	11	18	27	39	54	72	94	120	150	185	225	270	321	378	441	511	588

The total number of structurally isomeric alkenes of N carbon atoms may be obtained by a summation of the numbers calculated in Groups A, B, C and D. The actual meaning and use of these recursion type formulas may be illustrated in the calculation of the number of structurally isomeric tetradecylenes, since the hydrocarbons corresponding to $C_{14}H_{28}$ represent the simplest homologs of ethylene in which all structural types are represented.

SAMPLE CALCULATION

Group A. $N = 14;\ N - 2 = 12$

$T_{(N-2)} = 3057$

Group B. Even carbon content: number of terms is $(N-2)/2 = 6$

$$\begin{aligned}
2\cdot T_1\cdot T_{11} &= 2\cdot 1\cdot 1238 = 2476\\
2\cdot T_2\cdot T_{10} &= 2\cdot 1\cdot 507 = 1014\\
2\cdot T_3\cdot T_9 &= 2\cdot 2\cdot 211 = 844\\
2\cdot T_4\cdot T_8 &= 2\cdot 4\cdot 89 = 712\\
2\cdot T_5\cdot T_7 &= 2\cdot 8\cdot 39 = 624\\
2\cdot\frac{T_6\cdot(1+T_6)}{2} &= 2\cdot\frac{17\cdot 18}{2} = 306
\end{aligned}$$

Group C.

Type (1)

$3 \cdot T_9 \cdot T_2 \cdot T_1 = 3 \cdot 211 \cdot 1 \cdot 1 = 633$

$3 \cdot T_8 \cdot T_3 \cdot T_1 = 3 \cdot 89 \cdot 2 \cdot 1 = 534$

$3 \cdot T_7 \cdot T_4 \cdot T_1 = 3 \cdot 39 \cdot 4 \cdot 1 = 468$

$3 \cdot T_7 \cdot T_3 \cdot T_2 = 3 \cdot 39 \cdot 2 \cdot 1 = 234$

$3 \cdot T_6 \cdot T_5 \cdot T_1 = 3 \cdot 17 \cdot 8 \cdot 1 = 408$

$3 \cdot T_6 \cdot T_4 \cdot T_2 = 3 \cdot 17 \cdot 4 \cdot 1 = 204$

$3 \cdot T_5 \cdot T_4 \cdot T_3 = 3 \cdot 8 \cdot 4 \cdot 2 = 192$

Type (2)

$1/2 \cdot T_1 \cdot T_{10} \cdot (1 + 3T_1) = 1/2 \cdot 1 \cdot 507 \cdot (1 + 3.1) = 1014$

$1/2 \cdot T_2 \cdot T_8 \cdot (1 + 3T_2) = 1/2 \cdot 1 \cdot 89 \cdot (1 + 3.1) = 178$

$1/2 \cdot T_3 \cdot T_6 \cdot (1 + 3T_3) = 1/2 \cdot 2 \cdot 17 \cdot (1 + 3.2) = 119$

$1/2 \cdot T_5 \cdot T_2 \cdot (1 + 3T_5) = 1/2 \cdot 8 \cdot 1 \cdot (1 + 3.8) = 200$

Type (3)

$1/2 \cdot (T_4)^2 \cdot (1 + T_4) = 1/2 \cdot 4^2 \cdot (1 + 4) = 40$

Group D.

Type (1)

$3 \cdot T_6 \cdot T_3 \cdot T_2 \cdot T_1 = 3 \cdot 17 \cdot 2 \cdot 1 \cdot 1 = 102$

$3 \cdot T_5 \cdot T_4 \cdot T_2 \cdot T_1 = 3 \cdot 8 \cdot 4 \cdot 1 \cdot 1 = 96$

Type (2)

$1/2 \cdot T_1 \cdot T_8 \cdot T_2 \cdot (1 + 3T_1) = 1/2 \cdot 1 \cdot 89 \cdot 1 \cdot (1 + 3.1) = 178$

$1/2 \cdot T_1 \cdot T_7 \cdot T_3 \cdot (1 + 3T_1) = 1/2 \cdot 1 \cdot 39 \cdot 2 \cdot (1 + 3.1) = 156$

$1/2 \cdot T_1 \cdot T_6 \cdot T_4 \cdot (1 + 3T_1) = 1/2 \cdot 1 \cdot 17 \cdot 4 \cdot (1 + 3.1) = 136$

$1/2 \cdot T_2 \cdot T_7 \cdot T_1 \cdot (1 + 3T_2) = 1/2 \cdot 1 \cdot 39 \cdot 1 \cdot (1 + 3.1) = 78$

$1/2 \cdot T_2 \cdot T_5 \cdot T_3 \cdot (1 + 3T_2) = 1/2 \cdot 1 \cdot 8 \cdot 2 \cdot (1 + 3.1) = 32$

$1/2 \cdot T_3 \cdot T_5 \cdot T_1 \cdot (1 + 3T_3) = 1/2 \cdot 2 \cdot 8 \cdot 1 \cdot (1 + 3.2) = 56$

$1/2 \cdot T_3 \cdot T_4 \cdot T_2 \cdot (1 + 3T_3) = 1/2 \cdot 2 \cdot 4 \cdot 1 \cdot (1 + 3.2) = 28$

$1/2 \cdot T_4 \cdot T_3 \cdot T_1 \cdot (1 + 3T_4) = 1/2 \cdot 4 \cdot 2 \cdot 1 \cdot (1 + 3.4) = 52$

Type (3)

$1/2 \cdot (T_1)^2 \cdot T_9 \cdot (1 + T_1) = 1/2 \cdot 1^2 \cdot 211 \cdot (1 + 1) = 211$

$1/2 \cdot (T_2)^2 \cdot T_6 \cdot (1 + T_2) = 1/2 \cdot 1^2 \cdot 17 \cdot (1 + 1) = 17$

Type (4)

$i = (n - 2)/4 = (14 - 2)/4 = 3$

$1/8 \cdot T_3 \cdot (1 + T_3) \cdot [2 + T_3 \cdot (1 + T_3)] = 1/8 \cdot 2 \cdot (1 + 2) \cdot [2 + 2 \cdot (1 + 2)] = 6$

Type (5)

$1/4 \cdot T_5 \cdot T_1 \cdot (3 \cdot T_5 \cdot T_1 + T_5 + T_1 + 3) = 1/4 \cdot 8 \cdot 1 \cdot (3 \cdot 8 \cdot 1 + 8 + 1 + 3) = 72$

$1/4 \cdot T_4 \cdot T_2 \cdot (3 \cdot T_4 \cdot T_2 + T_4 + T_2 + 3) = 1/4 \cdot 4 \cdot 1 \cdot (3 \cdot 4 \cdot 1 + 4 + 1 + 3) = 20$

Thus, of the tetradecylenes there are 14,497 structural isomers. The totals of such structural isomers, as obtained by the use of these recursion formulas, through a carbon content of twenty are shown in Table II.[3]

TABLE II

NUMBER OF STRUCTURALLY ISOMERIC HYDROCARBONS OF THE ETHYLENE SERIES

Carbon content	Number of isomers	Carbon content	Number of isomers	Carbon content	Number of isomers
2	1	9	153	15	36,564
3	1	10	377	16	93,650
4	3	11	914	17	240,916
5	5	12	2,281	18	623,338
6	13	13	5.690	19	1,619.346
7	27	14	14.497	20	4.224,993
8	66				

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[3] The structural formulas of the homologs of ethylene, inclusive of a carbon content of eleven, were written in connection with the derivation of these recursion formulas. The totals obtained from actual count of these structural formulas agreed exactly with those derived by use of the recursion formulas.

Summary

By means of a separation of the isomeric hydrocarbons of the ethylene series 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 structurally isomeric homologs of ethylene and the alkyl groups which may be considered to be attached to the $>C{=}C<$ grouping. Mathematical formulas of the (finite) recursion type are advanced which permit of the calculation, from their carbon content, of the number of isomers in each of these structural types. In using these recursion formulas to calculate the total number of such structurally isomeric hydrocarbons of any given carbon content, the total number of alkyl groups (*i. e.*, the total number of structurally isomeric monosubstitution products of the paraffins) of $N-2$ and all lesser carbon contents must be known.

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Naphthol Studies. II. The Chlorination of 1,5-Dihydroxynaphthalene

BY ALVIN S. WHEELER AND W. J. MATTOX[1]

The studies of Wheeler and Ergle[2] have shown that one, two or three atoms of bromine may be introduced into 1,5-dihydroxynaphthalene. In the present study we have prepared dichloro and trichloro derivatives but no tetrachloro compound was obtained. A similar relation was noted in the juglone studies of Wheeler and co-workers,[3,4] more bromine being taken up than chlorine. Willstätter and Schuler[5] chlorinated dihydroxynaphthalene in acetic acid solution but for the purposes of this study we found it better to chlorinate the diacetate in carbon tetrachloride. The description of our compounds C and G does not agree with that of Willstätter and Schuler. This will be re-examined. In chlorinating the diacetate at room temperature two atoms of chlorine are taken up whereas at 80° three atoms are introduced. In each case one acetyl group is hydrolyzed. We tried to prove that OH and O in compound I are ortho to each other by Dimroth's pyroboroacetate ester method. We obtained the characteristic reddish purple color but no solid product. The first two chlorine atoms are put in positions 4 and 8 and the third also in 4 since one

[1] Extract from a thesis presented to the Faculty of the University of North Carolina by W. J. Mattox for the degree of Doctor of Philosophy in 1932.

[2] Wheeler and Ergle, THIS JOURNAL, **52**, 4873 (1930).

[3] Wheeler and Scott, *ibid.*, **41**, 834 (1919).

[4] Wheeler, Dawson and McEwen, *ibid.*, **45**, 1970 (1923).

[5] Willstätter and Schuler, *Ber.*, **61**, 362 (1928).