Reaction with Ethylmagnesium Bromide, β,β-Diphenyl Valerylmesitylene $C_2H_5C(C_6H_5)_2CH_2COC_6H_2(CH_3)_3$.—A solution of 5 g. of phenyl benzalacetomesitylene in 250 cc. of dry ether was added in the course of three hours to a solution of ethylmagnesium bromide prepared from 1.2 g. of magnesium. The color of the red intermediate compound was very persistent but it gradually faded to a light pink when the mixture was boiled for four hours. By decomposition with iced hydrochloric acid, and the usual manipulation of the ethereal layer, the mixture yielded a solid which separated from petroleum ether in needles and which melted at 106°.

Anal. Calcd. for $C_{26}H_{28}O$: C, 87.6; H, 7.9. Found: C, 87.4; H, 7.7.

β-Methyl Benzalacetomesitylene and Methylmagnesium Iodide, $(C_6H_5)(CH_3)_2CCH_2COC_6H_2(CH_3)_3$.—An ethereal solution of 5 g. of methyl benzalacetomesitylene was added in the course of a few minutes to an ethereal solution of methylmagnesium iodide which had been prepared from 1.8 g. of magnesium. The orange-colored solution soon began to deposit a colorless magnesium derivative. After ten minutes at the ordinary temperature it was decomposed with ice and acid in the usual manner. It yielded a solid which crystallized from acetic acid in colorless needles and which melted at 184–185°.

Anal. Calcd. for $C_{20}H_{24}O$: C, 85.8; H, 8.6. Found: C, 86.0; H, 8.8.

Summary

The former statement that β-phenyl benzalacetomesitylene does not add phenylmagnesium bromide is incorrect. Both β-phenyl and β-methyl benzalacetomesitylene add Grignard reagents, forming enolates of the corresponding saturated ketones.

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The Number of Stereoisomeric and Non-Stereoisomeric Alkines

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Since the number of structurally isomeric alkines[1] can be readily deduced from the number of structurally isomeric mono-substitution products of the paraffins,[2] an attempt has been made to calculate the number of stereoisomeric alkines.

Blair and Henze have advanced recursion formulas which[3] permit the calculation from their carbon content of the number of stereoisomeric and non-stereoisomeric primary, secondary and tertiary mono-substitution products of the paraffins. The use of these formulas depends upon the knowledge of the total number of stereoisomeric and non-stereoisomeric mono-substituted paraffins of every lower carbon content. By employing the published data of Blair and Henze, it is possible to calculate the number of stereoisomeric and non-stereoisomeric mono-substituted and

(1) Coffman, and Blair with Henze, THIS JOURNAL, **55**, 252 (1933).
(2) Henze and Blair, *ibid.*, **53**, 3042–3046 (1931).
(3) Blair and Henze, *ibid.*, **54**, 1098–1106 (1932).

di-substituted alkines of the formulas RC≡CH and RC≡CR′. The calculation depends upon the classification of the alkines into simple types whose number of stereoisomers may be estimated.

Mono-substituted Alkines.—The structural formulas of the mono-substituted alkines RC≡CH of N total carbon content may be formed by attaching to the residue —C≡CH each alkyl group R of $N-2$ carbon atoms. It is therefore apparent that the number of stereoisomeric mono-substituted alkines of N total carbon content formed in this way will equal the total number of stereoisomeric mono-substituted paraffins of all types containing $N-2$ carbon atoms. For these same reasons the number of non-stereoisomeric mono-substituted alkines of N total carbon content will equal the total number of non-stereoisomeric mono-substituted paraffins of all types containing $N-2$ carbon atoms. These values may be obtained from the tables of Blair and Henze.

Di-substituted Alkines.—The structural formulas of the di-substituted alkines RC≡CR′ of N total carbon content may be formed by attaching to the residue —C≡C— the alkyl groups R and R′ (the sum of the carbon atoms in R and R′ must always equal $N-2$). The total number of isomers that may be formed in this manner will be determined by the number of possibilities of combining with the residue —C≡C— complementary values of R and R′. These combinations may be divisible into two types: (1) in which R and R′ may be of[4] unequal carbon content, and (2) in which R and R′ may be of equal content. As a matter of fact, type (2) is impossible for RC≡CR′ of an odd number of carbon atoms since $(N-2)/2$ must be an integer, greater than zero.

Type I.—When R and R′ are of unequal carbon content, the number of possibilities of combining stereoisomeric and non-stereoisomeric values of R and R′ with the residue —C≡C— may be represented by the expression $A_{s_i} \cdot A_{s_j} + A_{s_i} \cdot A_{n_j} + A_{n_i} \cdot A_{s_j}$ in which A_{s_i} and A_{s_j} represent the total number of all types of stereoisomeric mono-substituted paraffins RX and R′X each of carbon contents i and j, and in which A_{n_i} and A_{n_j} represent the total number of all types of non-stereoisomeric mono-substituted paraffins RX and R′X each of carbon contents i and j. Here i and j are integers, distinct, and greater than zero, $i > j$, and $i + j = N-2$. By defining $T_i = A_{s_i} + A_{n_i}$ and $T_j = A_{s_j} + A_{n_j}$, substitution in and simplification of the above expression yields a formula representing the total number of stereoisomeric alkines RC≡CR′ of type 1

$$\Sigma(T_i T_j - A_{n_i} A_{n_j}) \qquad (I_s)$$

When N is even, the number of $T_i \cdot T_j - A_{n_i} \cdot A_{n_j}$ terms in the summation will be $(N-4)/2$; when N is odd, the number of terms will be $(N-3)/2$.

(4) These types are analogous to those of the secondary mono-substitution products of the paraffins as classified by Blair and Henze.

The number of non-stereoisomeric alkines RC≡CR′ of type 1 will be equal to

$$\Sigma A_{n_i} \cdot A_{n_j} \qquad (I_n)$$

requiring $(N-4)/2$ terms when N is even, and $(N-3/2)$ terms when N is odd.

Type II.—When R and R′ are of equal carbon content, it is convenient to subdivide the isomers further into two groups: (a) in which R and R′ are structurally and stereoisomerically identical, and (b) in which R and R′ are not identical.

Group (a).—The number of possibilities of combining identical stereoisomeric values of R and R′ with the residue —C≡C— will equal the number of stereoisomers of this subdivision, or A_{s_i}. By the combination of identical non-stereoisomeric values of R and R′ with the residue —C≡C—, no stereoisomers can result.

Group (b).—When non-identical complementary values of R and R′, both stereoisomeric and non-stereoisomeric, are combined with the residue —C≡C—, the number of such possibilities may be represented by the expression $A_{s_i} \cdot A_{n_i} + A_{s_i}(A_{s_i} - 1)/2$. The sum of the expressions in group (a) and group (b) gives a formula representing the total number of stereoisomers of type II.

$$A_{s_i}(2A_{n_i} + A_{s_i} + 1)/2 \qquad (II_s)$$

in which i is an integer greater than zero, and $i = (N-2)/2$.

TABLE I

ISOMERIC ALKINES

Carbon content	RC≡CH		RC≡CR′		RC≡CH and RC≡CR′		
	Stereo	Non-stereo	Stereo	Non-stereo	Total stereo	Total Non-stereo	Total isomers
3	0	1	0	0	0	1	1
4	0	1	0	1	0	2	2
5	0	2	0	1	0	3	3
6	2	3	0	3	2	6	8
7	6	5	2	5	8	10	18
8	20	8	8	11	28	19	47
9	60	14	30	19	90	33	123
10	176	23	101	38	277	61	338
11	512	39	316	68	828	107	935
12	1,488	65	975	129	2,463	194	2,657
13	4,326	110	2,948	232	7,274	342	7,616
14	12,648	184	8,878	428	21,526	612	22,138
15	37,186	310	26,622	768	63,808	1,078	64,886
16	109,980	520	79,980	1,393	189,960	1,913	191,873
17	327,216	876	240,590	2,487	567,806	3,363	571,169
18	979,020	1,471	726,238	4,460	1,705,258	5,931	1,711,189
19	2,944,414	2,475	2,199,070	7,924	5,143,484	10,399	5,153,883
20	8,897,732	4,159	6,683,108	14,095	15,580,840	18,254	15,599,094
21	27,004,290	6,996	20,378,720	24,925	47,383,010	31,921	47,414,931
22	82,287,516	11,759	62,347,546	44,065	144,635,062	55,824	144,690,886

The number of possibilities of combining non-stereoisomeric values of R and R′ (type II) with the residue —C≡C— may be represented by the expression $A_{n_i} + A_{n_i}(A_{n_i} - 1)/2$ which on simplification yields

$$A_{n_i}(A_{n_i} + 1)/2 \qquad (II_n)$$

representing the number of non-stereoisomeric alkines RC≡CR′ of type II.

The finite formulas I_s, I_n, II_s and II_n permit the calculation of the number of stereoisomeric and non-stereoisomeric di-substituted alkines RC≡CR′ of N total carbon content when the number of stereoisomeric and non-stereoisomeric mono-substitution products of the paraffins of all types of $N-3$ and every lower carbon content is known. In applying these formulas the values for the stereoisomeric and non-stereoisomeric mono-substitution products of the paraffins, as calculated by Blair and Henze, have been employed. The table indicates the calculated number of stereoisomeric and non-stereoisomeric alkines containing from three to twenty-two carbon atoms inclusive.[5]

Summary

The number of stereoisomeric and non-stereoisomeric mono-substituted alkines RC≡CH of N total carbon content has been deduced from the number of stereoisomeric and non-stereoisomeric mono-substitution products of the paraffins.

The number of stereoisomeric and non-stereoisomeric di-substituted alkines RC≡CR′ of N total carbon content has been calculated employing finite recursion formulas. The use of these formulas is dependent upon the knowledge of the number of stereoisomeric and non-stereoisomeric mono-substitution products of the paraffins of $N-3$ and every lower carbon content. The number of isomers so obtained agrees with the number required by theory through the decines as shown by writing the formulas and counting the stereoisomeric and non-stereoisomeric alkines RC≡CR′.

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(5) The number of stereoisomeric and non-stereoisomeric disubstituted alkines RC≡CR′, as represented in the table, agrees exactly with the number obtained by writing and counting the structural formulas inclusive of the decines RC≡CR′.