

and hydrochloric acid or by sodium amalgam and water gave neither the corresponding amine or hydrazine.

4. It is pointed out that there is no evidence that, as a rule, the true nitroso group in aliphatic compounds is reduced to the corresponding amine or hydroxylamine except in small yields.

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

THE NUMBER OF STEREOISOMERIC AND NON-STEREOISOMERIC PARAFFIN HYDROCARBONS

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No detailed attempt to relate the number of stereoisomeric and non-stereoisomeric paraffin hydrocarbons to their respective carbon contents is recorded in the chemical literature. Having first developed a mathematical relationship between carbon content and the number of structural isomers, both among the paraffin hydrocarbons¹ and their mono-substitution products,² the authors were successful in developing a series of recursion (finite) type formulas permitting the calculation of the number of stereoisomeric and non-stereoisomeric mono-substitution products of the paraffins³ from their carbon content. By utilizing a combination of the methods previously developed it is possible to derive analogous mathematical formulas by means of which the number of stereoisomeric and non-stereoisomeric paraffin hydrocarbons may be estimated accurately.

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

Group A. Even Carbon Content.—If two alkyl radicals of $N/2$ carbon atoms each are combined, a hydrocarbon of N carbon atoms is obtained,

¹ H. R. Henze and C. M. Blair, *THIS JOURNAL*, 53, 3077-3085 (1931).

² H. R. Henze and C. M. Blair, *ibid.*, 53, 3042-3046 (1931).

³ C. M. Blair with H. R. Henze, *ibid.*, 54, 1098 (1932).

and the number of stereoisomers that may be thus formed with and non-stereoisomeric alkyl stereoisomeric alkyl radicals themselves, no stereoisomers are present in the radicals and ever, when the non-stereoisomers are combined with the stereoisomers one stereoisomer is formed with of such combinations will be of stereoisomeric alkyl radicals number of non-stereoisomeric stereoisomeric alkyl radicals themselves, one stereoisomer is formed number of these combinations total number of stereoisomers

$As_{N/2}$

The number of non-stereoisomers

Group A. Odd Carbon
determining the number of stereoisomers of a group, it is necessary to re-
[1 + $As_{(N-1)/2}$] carbon atoms may be
carbon atoms by the add-
—CH₂— group. Hence, the
portions of the alkyls of $(N-1)/2$
with the alkyls of $(N-1)/2$
by joining the alkyls of $(N-1)/2$
carbon atoms through an
stereoisomers so formed
[1 + $As_{(N-1)/2}$]/2. The
will equal $An_{(N-1)/2}$ [1 +
remaining stereoisomeric and
the radicals, both stereoisomeric
carbon atoms will form
the expression [$As_{(N+1)/2}$
 $As_{(N-1)/2}$ + $An_{(N-1)/2}$].
combination of the remaining
with the stereoisomers of
the non-stereoisomers of (

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and the number of stereoisomeric and non-stereoisomeric hydrocarbons that may be thus formed will depend upon the number of stereoisomeric and non-stereoisomeric alkyl radicals of $N/2$ carbon atoms. If the non-stereoisomeric alkyl radicals of $N/2$ carbon atoms are combined with themselves, no stereoisomers are formed, for no asymmetric carbon atoms are present in the radicals and none are created by the combination. However, when the non-stereoisomeric alkyl radicals of $N/2$ carbon atoms are combined with the stereoisomeric alkyl radicals of $N/2$ carbon atoms, one stereoisomer is formed with each possible combination and the number of such combinations will equal $A_{S_{N/2}} \cdot A_{n_{N/2}}$, where $A_{S_{N/2}}$ is the number of stereoisomeric alkyl radicals of $N/2$ carbon atoms, and $A_{n_{N/2}}$ is the number of non-stereoisomeric alkyl radicals of $N/2$ carbon atoms. Likewise, for the remaining type of combination of group A, in which the stereoisomeric alkyl radicals of $N/2$ carbon atoms are combined with themselves, one stereoisomer is formed with each possible combination and the number of these combinations will be $A_{S_{N/2}} \cdot (1 + A_{S_{N/2}})/2$. Hence, the total number of stereoisomers of group A, for even carbon content, will equal

$$A_{S_{N/2}} \cdot A_{n_{N/2}} + \frac{A_{S_{N/2}}(1 + A_{S_{N/2}})}{2}$$

The number of non-stereoisomers of group A, for even carbon content, is

$$\frac{A_{n_{N/2}}(1 + A_{n_{N/2}})}{2}$$

Group A. Odd Carbon Content.—In order to prevent duplication in determining the number of stereoisomers and non-stereoisomers in this group, 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 $-\text{CH}_2-$ group. Hence, the hydrocarbons resulting from combining such portions 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 stereoisomers so formed will equal $A_{S_{(N-1)/2}} \cdot A_{n_{(N-1)/2}} + A_{S_{(N-1)/2}} \cdot [1 + A_{S_{(N-1)/2}}]/2$. The number of non-stereoisomers formed in this way will equal $A_{n_{(N-1)/2}} \cdot [1 + A_{n_{(N-1)/2}}]/2$. The combination of the remaining stereoisomeric alkyl radicals of $(N + 1)/2$ carbon atoms with the radicals, both stereoisomeric and non-stereoisomeric, of $(N - 1)/2$ carbon atoms will form that number of stereoisomers represented by the expression $[A_{S_{(N+1)/2}} - A_{S_{(N-1)/2}}] \cdot T_{(N-1)/2}$ where $T_{(N-1)/2} = A_{S_{(N-1)/2}} + A_{n_{(N-1)/2}}$. The number of stereoisomers formed upon combination of the remaining non-stereoisomers of $(N + 1)/2$ carbon atoms with the stereoisomers of $(N - 1)/2$ carbon atoms, for combination with the non-stereoisomers of $(N - 1)/2$ carbon atoms would result in the forma-

tion of no stereoisomers, may be expressed as $[An_{(N+1)/2} - An_{(N-1)/2}] \cdot As_{(N-1)/2}$.

Therefore, the total number of stereoisomers in group A, for odd carbon content, will equal

$$\left[An_{\left(\frac{N+1}{2}\right)} - An_{\left(\frac{N-1}{2}\right)} \right] \cdot As_{\left(\frac{N-1}{2}\right)} + T_{\left(\frac{N-1}{2}\right)} \cdot As_{\left(\frac{N+1}{2}\right)} - \frac{As_{\left(\frac{N-1}{2}\right)} \cdot \left[As_{\left(\frac{N-1}{2}\right)} - 1 \right]}{2}$$

The number of non-stereoisomers in group A, for odd carbon content, will be

$$\left[An_{\left(\frac{N+1}{2}\right)} - An_{\left(\frac{N-1}{2}\right)} \right] \cdot An_{\left(\frac{N-1}{2}\right)} + \frac{An_{\left(\frac{N-1}{2}\right)} \cdot \left[1 + An_{\left(\frac{N-1}{2}\right)} \right]}{2}$$

Group B.—If the graphic formula of a hydrocarbon 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 are attached to the specified carbon atom. The total number of stereoisomers and non-stereoisomers of group B will be obtained by a summation of the numbers in 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 of the branches were of the same carbon content and different from that of 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 stereoisomers and non-stereoisomers in each case may be calculated by the following mathematical formula of the (finite) recursion type for that particular case.⁴

⁴ The derivations of these formulas are exactly analogous to those for similar cases of the tertiary mono-substitution products of the paraffins which have been described by the authors *THIS JOURNAL*, 54, 1098 (1932).

Case (1)

Stereoisomers	$2\Sigma T_i \cdot T_j \cdot T_k$	(sa ₁)
Non-stereoisomers	None	(na ₁)

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)

Stereoisomers	$\Sigma\{(T_i)^2 - An_i\} \cdot T_j + An_i \cdot As_j\}$	(sa ₂)
Non-stereoisomers	$\Sigma An_i \cdot An_j$	(na ₂)

where $2i + j = N - 1$ 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)

Stereoisomers	$\frac{2T_i + (T_i)^2}{3} - (An_i)^2$	(sa ₃)
Non-stereoisomers	$(An_i)^2$	(na ₃)

where $3i = N - 1$; and 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 of the 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 that of the fourth; (4) in which all four branches are of the same carbon content; and (5) in which the four branches are 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, since in case (4) $(N - 1)$ must be divisible by four, and in case (5) $(N - 1)$ must be divisible by two. The number of stereoisomers and non-stereoisomers in each case may be calculated by the following mathematical formula of the (finite) recursion type for that particular case.

Case (1)

Stereoisomers	$2\Sigma T_h \cdot T_i \cdot T_j \cdot T_k$	(sb ₁)
Non-stereoisomers	None	(nb 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)

Stereoisomers

$$\Sigma\{[(T_i)^2 - An_i] \cdot T_j T_k + An_i \cdot As_j T_k + An_i \cdot An_j \cdot As_k\} \quad (sb_2)$$

Non-stereoisomers

$$\Sigma An_i \cdot An_j \cdot An_k \quad (nb_2)$$

where $2i + j + k = N - 1$; and i, j and k are integers, distinct, and greater than zero.

Case (3)

Stereoisomers

$$\Sigma\left\{\left[\frac{2T_i + (T_i)^3}{3} - (An_i)^2\right] \cdot T_j + (An_i)^2 \cdot As_j\right\} \quad (sb_3)$$

Non-stereoisomers

$$(An_i)^2 \cdot An_j \quad (nb_3)$$

where $3i + j = N - 1$; and i and j are integers, distinct, and greater than zero.

Case (4)

Stereoisomers

$$\frac{(T_i)^4 + 11(T_i)^2 - 6An_i[1 + (An_i)^2]}{12} \quad (sb_4)$$

Non-stereoisomers

$$\frac{An_i[1 + (An_i)^2]}{2} \quad (nb_4)$$

where $4i = N - 1$; and i is an integer greater than zero.

Case (5)

Stereoisomers

$$\frac{1}{2}\Sigma[(T_i T_j)^2 + T_i T_j - An_i \cdot An_j \cdot (An_i + An_j)] \quad (sb_5)$$

Non-stereoisomers

$$\frac{An_i \cdot An_j \cdot (An_i + An_j)}{2} \quad (nb_5)$$

where $2i + 2j = N - 1$; i and j are integers, distinct, and greater than zero; and $i > j$.

The total number of stereoisomeric and non-stereoisomeric hydrocarbons of N carbon atoms may be determined by adding to the number of stereoisomers and non-stereoisomers 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 formulas⁵ may be illustrated in the calculation of the number of stereoisomeric and non-stereoisomeric tetradecanes.

⁵ In using these recursion formulas to calculate the total number of isomeric paraffins of any specified carbon content it is necessary to make a preliminary calculation of the total number of stereoisomeric and non-stereoisomeric mono-substitution products of the paraffins of $N/2$ and lesser carbon contents. The totals for such isomers through C_{20} are recorded in Table I, THIS JOURNAL, 54, 1105 (1932).

Sample Calculation⁶Group A. $N = 14$; $N/2 = 7$

Stereoisomers

$$As_7 \cdot An_7 + As_7(1 + As_7)/2 = 60.14 + 60(1 + 60)/2 = 2670$$

Non-stereoisomers

$$An_7(1 + An_7)/2 = 14(1 + 14)/2 = 105$$

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

Type (a)

Case (1)

Stereoisomers

$$2 \cdot T_6 \cdot T_6 \cdot T_2 = 2 \cdot 28 \cdot 11 \cdot 1 = 616$$

$$2 \cdot T_6 \cdot T_4 \cdot T_3 = 2 \cdot 28 \cdot 5 \cdot 2 = 560$$

Non-stereoisomers

There can be no non-stereoisomers of this type

Case (2)

Stereoisomers

$$(T_6^2 - An_6)T_1 + An_6 \cdot As_1 = (28^2 - 8)1 + 8 \cdot 0 = 776$$

$$(T_5^2 - An_5)T_3 + An_5 \cdot As_3 = (11^2 - 5)2 + 5 \cdot 0 = 232$$

$$(T_4^2 - An_4)T_6 + An_4 \cdot As_6 = (5^2 - 3)11 + 3 \cdot 6 = 260$$

Non-stereoisomers

$$An_6 \cdot An_1 = 8 \cdot 1 = 8$$

$$An_3 \cdot An_3 = 5 \cdot 2 = 10$$

$$An_4 \cdot An_5 = 3 \cdot 5 = 15$$

Case (3)

This case is not actually possible for this carbon content

Type (b)

Case (1)

Stereoisomers

$$2 \cdot T_5 \cdot T_4 \cdot T_2 \cdot T_1 = 2 \cdot 28 \cdot 5 \cdot 1 \cdot 1 = 280$$

$$2 \cdot T_5 \cdot T_4 \cdot T_3 \cdot T_1 = 2 \cdot 11 \cdot 5 \cdot 2 \cdot 1 = 220$$

Non-stereoisomers

There can be no non-stereoisomers of this type

Case (2)

Stereoisomers

$$(T_5^2 - An_5)T_2 \cdot T_1 + An_5 \cdot As_2 \cdot T_1 + An_5 \cdot An_2 \cdot As_1 = (11^2 - 5)1 \cdot 1 + 5 \cdot 0 \cdot 1 + 5 \cdot 1 \cdot 0 = 116$$

$$(T_4^2 - An_4)T_3 \cdot T_2 + An_4 \cdot As_3 \cdot T_2 + An_4 \cdot An_2 \cdot As_2 = (5^2 - 3)2 \cdot 1 + 3 \cdot 0 \cdot 1 + 3 \cdot 2 \cdot 0 = 44$$

$$(T_3^2 - An_3)T_6 \cdot T_1 + An_3 \cdot As_6 \cdot T_1 + An_3 \cdot An_6 \cdot As_1 = (2^2 - 2)28 \cdot 1 + 2 \cdot 20 \cdot 1 + 2 \cdot 8 \cdot 0 = 96$$

$$(T_3^2 - An_3)T_6 \cdot T_2 + An_3 \cdot As_6 \cdot T_2 + An_3 \cdot An_6 \cdot As_2 = (2^2 - 2)11 \cdot 1 + 2 \cdot 6 \cdot 1 + 2 \cdot 5 \cdot 0 = 34$$

$$(T_2^2 - An_2)T_6 \cdot T_3 + An_2 \cdot As_6 \cdot T_3 + An_2 \cdot An_6 \cdot As_3 = (1^2 - 1)28 \cdot 2 + 1 \cdot 20 \cdot 2 + 1 \cdot 8 \cdot 0 = 40$$

$$(T_2^2 - An_2)T_6 \cdot T_4 + An_2 \cdot As_6 \cdot T_4 + An_2 \cdot An_6 \cdot As_4 = (1^2 - 1)11 \cdot 5 + 1 \cdot 6 \cdot 5 + 1 \cdot 5 \cdot 2 = 40$$

$$(T_1^2 - An_1)T_6 \cdot T_5 + An_1 \cdot As_6 \cdot T_5 + An_1 \cdot An_6 \cdot As_5 = (1^2 - 1)28 \cdot 11 + 1 \cdot 20 \cdot 11 + 1 \cdot 8 \cdot 6 = 268$$

⁶ The number of terms actually present in all theoretically possible cases of types (a) and (b) through $C_{10}H_{22}$ are recorded in Table I, THIS JOURNAL, 53, 3084 (1931).

Non-stereoisomers

$$\begin{aligned}
 An_3 \cdot An_2 \cdot An_1 &= 5 \cdot 1 \cdot 1 = 5 \\
 An_4 \cdot An_3 \cdot An_2 &= 3 \cdot 2 \cdot 1 = 6 \\
 An_3 \cdot An_5 \cdot An_1 &= 2 \cdot 8 \cdot 1 = 16 \\
 An_3 \cdot An_5 \cdot An_2 &= 2 \cdot 5 \cdot 1 = 10 \\
 An_2 \cdot An_6 \cdot An_3 &= 1 \cdot 8 \cdot 2 = 16 \\
 An_2 \cdot An_6 \cdot An_4 &= 1 \cdot 5 \cdot 3 = 15 \\
 An_1 \cdot An_6 \cdot An_6 &= 1 \cdot 8 \cdot 5 = 40
 \end{aligned}$$

Case (3)

Stereoisomers

$$[(2 \cdot T_4 + T_4^3)/3 - T_4^2]T_1 + An_4^2 \cdot As_1 = [(2 \cdot 5 + 5^3)/3 - 3^2] \cdot 1 + 3^2 \cdot 0 = 36$$

$$[(2 \cdot T_3 + T_3^3)/3 - T_3^2]T_4 + An_3^2 \cdot As_4 = [(2 \cdot 2 + 2^3)/3 - 2^2] \cdot 5 + 2^2 \cdot 2 = 8$$

Non-stereoisomers

$$An_3^2 \cdot An_1 = 3^2 \cdot 1 = 9$$

$$An_3^2 \cdot An_4 = 2^2 \cdot 3 = 12$$

Thus, of the tetradeccanes there are 6296 stereoisomers and 267 non-stereoisomers.

The number of stereoisomeric and non-stereoisomeric paraffins, as calculated by the use of these recursion type formulas, through the eicosanes is shown in Table I. It should be noted that these formulas were derived solely by adaptation of the theoretical considerations utilized in the three previous contributions of this series. Having made the calculations recorded in Table I, the respective totals of the series CH_4 to $C_{14}H_{30}$ were checked by actually writing the various structural formulas and counting the number of stereoisomers and non-stereoisomers occasioned by the presence of asymmetric and pseudo-asymmetric carbon atoms. The numbers so obtained agreed exactly with those predicted by the above calculations.

TABLE I

NUMBER OF STEREOISOMERIC AND NON-STEREOISOMERIC PARAFFIN HYDROCARBONS

Carbon content	Stereoisomers	Non-stereoisomers	Total	Carbon content	Stereoisomers	Non-stereoisomers	Total
1	0	1	1	11	290	55	345
2	0	1	1	12	804	96	900
3	0	1	1	13	2,256	156	2,412
4	0	2	2	14	6,296	267	6,563
5	0	3	3	15	17,689	433	18,122
6	0	5	5	16	49,952	747	50,699
7	4	7	11	17	142,016	1,239	143,255
8	11	13	24	18	406,330	2,089	408,419
9	35	20	55	19	1,169,356	3,498	1,172,854
10	101	35	136	20	3,390,052	5,912	3,395,964

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Summary

1. 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 stereoisomeric and non-stereoisomeric paraffins and the alkyl groups of which the former may be considered to be composed. Mathematical formulas of the recursion (finite) type are advanced which permit of the calculation, from their carbon content, of the number of stereoisomeric and non-stereoisomeric paraffins in each of these structural types. In using these recursion formulas to calculate the total of such isomers of any specified carbon content, the total number of stereoisomeric and non-stereoisomeric alkyl groups of $N/2$ and all lesser carbon contents must be known.

2. The total number of isomers so obtained agrees exactly through the tetradecanes with the numbers required by theory as tested by actually writing the structural formulas and counting the number of stereoisomers and non-stereoisomers.

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PREPARATION OF 1,2,3,4-TETRABROMOBUTANE

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One of the methods described in the literature for the laboratory preparation of 1,3-butadiene is that of Harries,¹ in which 2,3-dibromobutane is decomposed by soda lime at 600°. Although this method does not yield pure butadiene, the latter can be obtained by converting the impure product into 1,2,3,4-tetrabromobutane, and then reducing this compound with zinc and alcohol according to the method of Thiele.² The tetrabromo compound therefore represents a convenient source of pure butadiene. In connection with a problem requiring rather large amounts of butadiene, a modification of Harries' method was employed as a preparative procedure for 1,2,3,4-tetrabromobutane. As a result, considerable data were collected and several changes in the apparatus and procedure were made which render the method somewhat more reliable and convenient.³

The original Harries method involved dropping 2,3-dibromobutane upon soda-lime contained in an iron pot at 600°. The butadiene and

¹ Harries, *Ann.*, 383, 176 and 181 (1911).

² Thiele, *ibid.*, 308, 333 (1899); Birch, *Ind. Eng. Chem.*, 20, 474 (1928); Farmer, Lawrence and Thorpe, *J. Chem. Soc.*, 729 (1928).

³ Recently Muskat and Northrup [THIS JOURNAL, 52, 4050 (1930)], have described a laboratory method of preparing butadiene which involves the following operations: (1) converting butyl alcohol into butyl chloride, (2) chlorinating butyl chloride to dichlorobutane and (3) converting dichlorobutane into butadiene by passing it over heated soda-lime.