4. 2,3,4,6-Tetramethyl-*d*-glucoseen-1,2 is not a probable intermediate in the epimerization of tetramethylglucopyranose.

5. An improved preparation of 2,3,4,6-tetramethyl-*d*-glucoseen-1,2 is recorded.

6. Tetramethyl-*d*-mannopyranose-1(α)-acetate has been synthesized in crystalline condition.

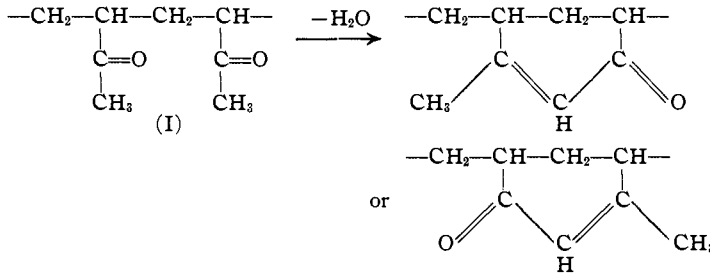
COLUMBUS, OHIO RECEIVED OCTOBER 3, 1941

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Intramolecular Condensations in Polymers*

BY FREDERICK T. WALL

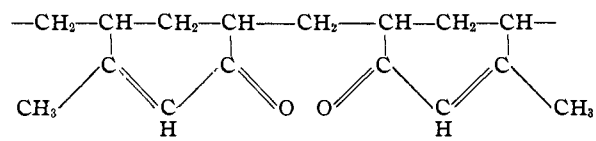
Recent experimental investigations by Marvel and co-workers[1] have shown that polymers of the type formed from methyl vinyl ketone can undergo intramolecular aldol condensations upon heating. The reaction which takes place can be illustrated for a portion of the polymers as follows:



(I) (II) (III)

If the condensations were to continue down the entire length of the polymer chain according to only one of the patterns, II or III, then all of the oxygen save one end atom would be eliminated. Experimentally[1] it was found that the elimination of oxygen was far from complete so the question naturally arose as to the reason.

The failure to eliminate nearly all of the oxygen upon heating can be explained qualitatively in the following way. Supposing that the condensations take place in accordance with either of the patterns II or III, it is seen that pairs of carbonyls will ultimately face each other at various places along the chain



(IV)

Since the oxygens of such pairs of carbonyls cannot enter into condensation reactions, they must remain in the polymer. Assuming that the condensations take place in a perfectly random way, the amount of oxygen that can be expected to remain in a polymer is simply a matter of probability and statistics.

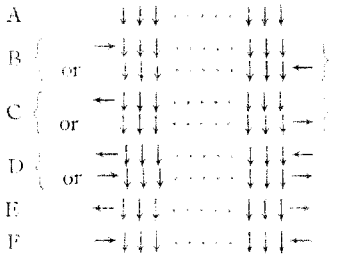
The statistical problem involved here is similar to but not identical with one considered by Flory and others.[2] Flory was concerned with the removal of pairs of substituents from vinyl polymers. The difference between that problem and the present one is that in the former a given substituent could react (be removed) only once, whereas in the present instance a given acetyl group might react twice, once through its carbonyl and once through its methyl group. Three cases of the problem will be considered. First it will be assumed that all of the acetyl groups are situated 1–3 with respect to their nearest neighbors. This is the so-called "head to tail" polymer. Next the problem will be treated on the assumption that the vinyl units are oriented at random, giving rise to 1–2, 1–3 and 1–4 linkages. Finally there will be considered the case for which the vinyl units are linked up alternately "head to head" and "tail to tail," giving rise to alternating 1–2 and 1–4 linkages. For each of the problems it will be assumed that an intramolecular condensation can occur only between two acetyl groups which are removed from each other by not more than three carbon atoms, and that not more than one condensation can occur between a given pair of acetyls. It will further be supposed that all condensations compatible with the above assumptions can take place with equal probability.

* Since the preparation of this manuscript, a note by P. J. Flory [THIS JOURNAL, **64**, 177 (1942)] has come to the author's attention. In this note, Flory treats one of the problems considered in the present paper, but by a different method. The present treatment permits immediate extension to random polymers and to copolymers which could not be done by Flory's method.

(1) (a) C. S. Marvel and C. S. Levesque, THIS JOURNAL, **60**, 280 (1938); (b) C. S. Marvel, E. H. Riddle and J. O. Corner, *ibid.*, **64**, 92 (1942).

(2) (a) P. J. Flory, *ibid.*, **61**, 1518 (1939); (b) F. T. Wall, *ibid.*, **62**, 803 (1940); (c) F. T. Wall, *ibid.*, **63**, 821 (1941); (d) R. Simha, *ibid.*, **63**, 1479 (1941).

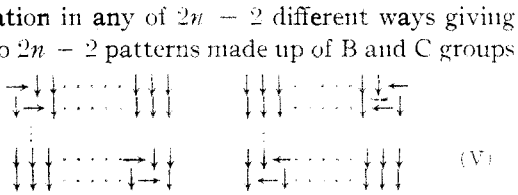
A. Head to Tail Polymers.—Before proceeding with the actual computations it is convenient to introduce some simplifying notation. First of all, a monomer unit with an unreacted carbonyl will be denoted by an arrow pointing downward, thus, ↓. Next a monomer unit whose carbonyl has reacted with a group to its right or left will be denoted by → or ←, respectively. With this notation, patterns, I, II, III and IV would be represented by ↓ ↓, → ↓, ↓ ←, and → ↓ ↓ ←. It will now be recognized that continuous groups of unreacted carbonyls can occur in any of six different patterns which will be represented as



An A group obviously is a polymer in which no reaction has yet occurred. After some condensations have taken place, B or C groups will appear at the ends of a polymer chain and D, E, or F groups within a polymer chain. The B, C, and D groups each appear to have two representations, but since the patterns are mirror images of each other they are really equivalent.

Let us define A_n, B_n, C_n, D_n, E_n, and F_n as the statistical number of oxygen atoms remaining after condensation possibilities are exhausted for the corresponding groups originally containing n free carbonyls. By an extension of Flory's method[2a] the values of A_n, etc., will now be calculated.

Evidently an A_n group can undergo its first condensation in any of $2n - 2$ different ways giving rise to $2n - 2$ patterns made up of B and C groups



(V)

Assuming each of the patterns in the array (V) to be equally probable it is seen that

$$(2n-2)A_n = 2B_{n-1} + 2(C_1 + B_{n-2}) + 2(C_2 + B_{n-3}) + \cdots + 2(C_{n-2} + B_1)$$

Simplifying the above equation yields

$$(n-1)A_n = \sum_{i=1}^{n-1} B_i + \sum_{i=1}^{n-2} C_i \qquad (1a)$$

In similar manner it can be shown that

$$(2n-3)B_n = \sum_{i=1}^{n-1} B_i + \sum_{i=1}^{n-3} C_i + \sum_{i=1}^{n-2} D_i + \sum_{i=2}^{n-1} F_i \qquad (1b)$$

$$(2n-1)C_n = \sum_{i=1}^{n-1} B_i + \sum_{i=1}^{n-1} C_i + \sum_{i=1}^{n-1} D_i + \sum_{i=1}^{n-2} E_i \qquad (1c)$$

$$(2n-2)D_n = 2\sum_{i=1}^{n-1} D_i + \sum_{i=1}^{n-3} E_i + \sum_{i=2}^{n-1} F_i \qquad (1d)$$

$$nE_n = \sum_{i=1}^{n-1} D_i + \sum_{i=1}^{n-1} E_i \qquad (1e)$$

$$(n-2)F_n = \sum_{i=1}^{n-3} D_i + \sum_{i=2}^{n-1} F_i \qquad (1f)$$

Replacing n by $n + 1$ in each of equations (1a) to (1f) and then subtracting from each the corresponding equation in n, the following new equations are obtained

$$nA_{n+1} - (n-1)A_n = B_n + C_{n-1} \qquad (2a)$$

$$(2n-1)B_{n+1} - (2n-3)B_n = B_n + C_{n-1} + D_{n-1} + F_n \quad n \geq 2 \qquad (2b)$$

$$(2n+1)B_{n+1} - (2n-1)C_n = B_n + C_n + D_n + E_{n-1} \qquad (2c)$$

$$2nD_{n+1} - (2n-2)D_n = 2D_n + E_{n-1} + F_n \quad n \geq 2 \qquad (2d)$$

$$(n+1)E_{n+1} - nE_n = D_n + E_n \qquad (2e)$$

$$(n-1)F_{n+1} - (n-2)F_n = D_{n-2} + F_n \quad n \geq 2 \qquad (2f)$$

By eliminating D terms from (2e) and (2f) it can be shown after a little manipulation that

$$E_{n+1} - E_n = F_{n+1} - F_{n-1} = \cdots = F_2 - E_0$$

Noting that $F_2 = 2$ and $E_0 = 0$, it follows that

$$F_{n+1} = E_n + 2 \qquad (3)$$

With the aid of equation (3), E_n and F_n terms can be eliminated from (2d) and (2f) to give a recurrence relation for D_n, namely

$$n(n-1)(n+1)D_{n+1} - (n-1)(2n+1)D_{n-1} + n(n-1)D_n - D_{n-2} = 0 \qquad (4)$$

Now it is obvious that $D_0 = D_1 = D_2 = 0$. Hence, by (2d) it is seen that $D_3 = 1/2$. Knowing these values to start with, it becomes possible to calculate the value of any D_n by successive application of the recurrence relation (4). This method is not practical, however, for large values of n, so another approach will be employed.

The procedure to be adopted consists of finding a generating function for D_n. First define

$$u(x) = \sum_{i=1}^{\infty} D_i x^i \qquad (5)$$

We shall now find a differential equation which has $u(x)$ for a solution in series. If we can then

obtain a general solution in closed form for the same differential equation, that solution with proper constants of integration can be equated to the series solution, thus providing the desired generating function.

It can be proved by direct substitution that the following differential equation has $u(x)$ for a series solution:

$$(1-x)^2\frac{d^2u}{dx^2} - \frac{3(1-x)}{x}\frac{du}{dx} + \frac{(3-2x-x^4)}{x^2}u = 0 \tag{6}$$

But eq. (6) has an exact solution in closed form, namely

$$u = \frac{ax}{(1-x)^2}e^{-x} + bxe^x \tag{7}$$

where a and b are arbitrary constants. In order that eq. (7) expanded in a power series be identical with eq. (5), it is necessary that $a = {}^1/_2$ and $b = -{}^1/_2$, taking cognizance of the fact that $D_1 = D_2 = 0$ and $D_3 = {}^1/_2$. Hence

$$u(x) = \sum_{i=1}^{\infty} D_i x^i \equiv \frac{xe^{-x}}{2(1-x)^2} - \frac{xe^x}{2} \tag{8}$$

Since D_n can differ from A_n only by a finite amount, it is clear that

$$\lim_{n\to\infty}\frac{D_n}{n} = \lim_{n\to\infty}\frac{A_n}{n} = f \tag{9}$$

where f is the fraction of oxygen remaining in an infinitely long polymer after condensation is complete. But from eq. (8) it is seen that

$$D_n = 1/2\left\{n - \frac{(n-1)}{1!} + \frac{(n-2)}{2!} - \ldots + \frac{(-1)^{n-2}\cdot 2}{(n-2)!} + \frac{(-1)^{n-1}-1}{(n-1)!}\right\} \tag{10}$$

and

$$\frac{D_n}{n} = \frac{1}{2}\left\{1 - \frac{\left(1-\frac{1}{n}\right)}{1!} + \frac{\left(1-\frac{2}{n}\right)}{2!} - \ldots + \frac{(-1)^{n-2}\cdot 2}{(n-2)!n} + \frac{(-1)^{n-1}-1}{(n-1)!n}\right\} \tag{11}$$

Therefore

$$f = \lim_{n\to\infty}\frac{D_n}{n} = \frac{1}{2}\left\{1 - \frac{1}{1!} + \frac{1}{2!} - \frac{1}{3!} + \ldots\right\} = \frac{e^{-1}}{2} \tag{12}$$

Thus it is seen that the fraction of the oxygen that can be expected to remain after heating an infinitely long polymer of the methyl vinyl ketone type is $1/2e$ or 18.39%.

By methods similar to those used above, generating functions for E_n and F_n can also be established. These turn out to be

$$v(x) = \sum_{i=1}^{\infty} E_i x^i \equiv \frac{e^{-x}}{2(1-x)^2} + \frac{e^{-x}}{2} - \frac{1}{1-x} \tag{13}$$

and

$$w(x) = \sum_{i=2}^{\infty} F_i x^i \equiv \frac{x^2e^{-x}}{2(1-x)^2} + \frac{x^2e^x}{2} + \frac{x^2}{1-x} \tag{14}$$

In order to complete the investigation it is still necessary to find A_n, or what is equivalent, the generating function for A_n. To do this, first rewrite eq. (1b) in terms of $n+1$ and subtract eq. (1c) from it term by term. The result is

$$(2n-1)(B_{n+1} - C_n) = B_n - C_{n-1} + F_2 + (F_3 - E_1) + (F_4 - E_2) + \ldots (F_n - E_{n-2})$$

Making use of eq. (3) this becomes

$$(2n-1)(B_{n+1} - C_n) = B_n - C_{n-1} + 2(n-1) \tag{15}$$

Noting that $B_2 - C_1 = B_1 - C_0 = 1$, it can be proved by induction with eq. (15) that

$$B_{n+1} = C_n + 1 \tag{16}$$

Define

$$y(x) = \sum_{i=1}^{\infty} A_i x^i \tag{17}$$

$$z(x) = \sum_{i=1}^{\infty} B_i x^i \tag{18}$$

$$t(x) = \sum_{i=1}^{\infty} C_i x^i \tag{19}$$

By reason of (16) it follows that

$$z = tx + \frac{x}{1-x} \tag{20}$$

But by (2b) it can be shown that

$$2(1-x)\frac{dz}{dx} + \left(2 - \frac{3}{x}\right)z = x^2t + xu + w - 1 + x \tag{21}$$

Eliminating t, u, and w from (21) by means of (20), (8) and (14), there is obtained

$$2(1-x)\frac{dz}{dx} - \frac{(x^2-2x+3)}{x}z = \frac{x^2e^{-x}}{(1-x)^2} - 1 + x \tag{22}$$

The solution of (22) is

$$z = \frac{x^{3/2}e^{-x/2}}{2(1-x)}\phi(x) + \frac{x}{1-x} + \frac{cx^{3/2}e^{-x/2}}{1-x} \tag{23}$$

where c is an arbitrary constant and where

$$\phi(x) = \int \frac{x^{1/2}e^{-x/2}}{(1-x)^2}\,dx \text{ with } \phi(0) = 0 \tag{24}$$

The function $\phi(x)$ can be expanded in the following form:

$$\phi(x) = \frac{2x^{1/2}e^{-x/2}}{3(1-x)}\left\{1 + \frac{2}{5}x + \frac{3}{5\cdot 7}x^2 + \frac{4}{5\cdot 7\cdot 9}x^3 \ldots\right\} \tag{25}$$

In order that (23) be identical with (18), it is necessary that $c = 0$, so

$$z(x) = \sum_{i=1}^{\infty} B_i x^i \equiv \frac{x^{3/2}e^{-x/2}}{2(1-x)}\phi(x) + \frac{x}{1-x} \tag{26}$$

Also from (20) it is seen that

$$f(x) = \sum_{i=1}^{\infty} C_i x^i = \frac{x^{1/2} e^{-x/2}}{2(1-x)} \phi(x) \qquad (27)$$

Now from eq. (1a) it can be shown that

$$(1-x)\frac{dy}{dx} - \frac{(1-x)}{x} y = z + fx \qquad (28)$$

Eliminating z and f by means of eqs. (26) and (27), eq. (28) can be solved to give the solution

$$y = \frac{x}{2}[\phi(x)]^2 + \frac{x}{1-x} + gx \qquad (29)$$

where g is the integration constant. To make (29) identical with (17), g must equal zero, so

$$y = \sum_{i=1}^{\infty} A_i x^i = \frac{x}{2}[\phi(x)]^2 + \frac{x}{1-x} \qquad (30)$$

or

$$y = x + x^2 + x^3 + \frac{11}{9}x^4 + \frac{7}{5}x^5 + \frac{832}{525}x^6 + \ldots \qquad (31)$$

B. Random Polymers and "Head to Head–Tail to Tail" Polymers.—Assuming condensations between 1–2 and 1–3 pairs are equally probable but that condensations between 1–1 or more widely separated pairs are not allowed, it is possible to calculate the fraction (f') of oxygen that can be expected to remain in a randomly oriented polymer. Using the results of Flory[2a] this fraction turns out to be

$$f' = \sum_{n=1}^{\infty} A_n (n-1)(1/2)^{n-2} \qquad (32)$$

But from (17) it is seen that

$$\frac{d}{dx}\left(\frac{y}{x}\right) = \sum_{n=1}^{\infty} (n-1) A_n x^{n-2} \qquad (33)$$

Hence

$$x^4 \frac{d}{dx}\left(\frac{y}{x}\right) = \sum_{n=1}^{\infty} (n-1) A_n x^{n-2} \qquad (34)$$

Letting $x = 1/2$ in (34), there is obtained

$$\left[x^4 \frac{d}{dx}\left(\frac{y}{x}\right)\right]_{x=1/2} = \sum_{n=1}^{\infty} A_n (n-1)(1/2)^{n-2} = f' \qquad (35)$$

Making use of (30) and (25) it is found that

$$f' = \left[\frac{2x^3 e^{-x}}{3(1-x)^3}\left(1 + \frac{2}{5}x + \frac{3}{5\cdot 7}x^2 + \ldots + \frac{x^3}{(1-x)^2}\right)\right]_{x=1/2} = 0.3118 \qquad (36)$$

Thus it is seen that the amount of oxygen that can be expected to remain in an infinitely long random polymer is 31.18%.

If the polymer has a "head to head–tail to tail" structure, then a third result is obtained. No involved calculation is necessary to see that 50% of the oxygen can be expected to remain in this case, since each 1–2 pair can eliminate one of its oxygens and 1–4 pairs cannot react.

C. Condensations in Copolymers.—Although no quantitative experiments on intramolecular condensations in copolymers have yet been reported, the statistical problem will nevertheless be treated briefly. It will be assumed that the copolymer is a "true copolymer"[3] and that it is made up of two kinds of vinyl units only one of which can be involved in the condensations here considered.

An exact treatment of this problem would take into account the finite chain lengths of the copolymers, a procedure which was adopted by R. Simha[2d] in connection with removal of substituents. Simha's method would become exceedingly complex in two of the three cases here considered, so a simplifying assumption will be made to the effect that the polymer chains are infinitely long.

Using a formula derived in an earlier publication[2b] the fraction of oxygen remaining in a long "head to tail" copolymer is seen to be

$$f = \sum_{n=1}^{\infty} A_n (1-x)^2 x^{n-1} \qquad (37)$$

In this equation x is the mole fraction of vinyl units in the polymer which are of the type capable of undergoing condensations. A_n is just the oxygen expectancy of an A group containing n members.

Comparing (37) with (17) it is seen that

$$f = \frac{(1-x)^2}{x} y \qquad (38)$$

where y is the generating function for A_n. Substituting for y there is obtained

$$f = \frac{2x^3 e^{-x}}{9}\left(1 + \frac{2}{5}x + \frac{3}{5\cdot 7}x^2 + \ldots + \frac{1}{\lfloor n}\right) + 1 - x \qquad (39)$$

or

$$f = 1 - x + \frac{2}{9}x^3 + \ldots \qquad (40)$$

Equation (39) gives the fraction as a function of the composition of the copolymer. As would be expected, $f = 1$ when $x = 0$. Also when $x = 1$, $f = 1/2e$ in agreement with (12). To get this result from (39) it should be noted that the series

(3) A "true copolymer" is one whose chains each have essentially the same composition as the average of all the chains. See F. T. Wall, THIS JOURNAL, **63**, 1862 (1941), for a discussion of the full significance of the term.

in braces which appears in that equation converges to 3/2 for $x = 1$.

Turning now to the random copolymer, it is seen from a previously derived formula[2b] that

$$f' = \sum_{n=0}^{\infty} \frac{(n+2)}{2^{n+1}} (\Delta_{n+1} - \Delta_n)x^n \qquad (41)$$

where $\Delta_n = A_n - A_{n-1}$ and f' is the fraction of oxygen remaining, it likewise being a function of the mole fraction x. But rearrangement of (37) shows that

$$f\left(\frac{x}{2}\right) = \sum_{n=0}^{\infty} (\Delta_{n+1} - \Delta_n)\left(\frac{x}{2}\right)^n \qquad (42)$$

Working with eq. (42) it can be shown that

$$f' = \left(\frac{x}{2}\right)\frac{\mathrm{d}}{\mathrm{d}x} f\left(\frac{x}{2}\right) + f\left(\frac{x}{2}\right) \qquad (43)$$

The explicit formula for f' will not be developed here but in series it starts out as follows

$$f' = 1 - \frac{3}{4}x + \frac{5}{72}x^3 + \ldots \qquad (44)$$

Evidently when $x = 0, f' = 1$. Also when $x = 1$, $f' = 0.3118\ldots$ as calculated previously.

Finally we shall consider the case of the regularly alternating 1–2, 1–4 copolymer. In this event it can readily be established that A_n'', the oxygen expectancy in a "head to head–tail to tail" group of length n is equal to $(n + 1)/2$. Hence

$$'' = \sum_{n=1}^{\infty} A_n''(1 - x)^2 x^{n-1} = \sum_{n=1}^{\infty} \left(\frac{n+1}{2}\right)(1 - x)^2 x^{n-1} \qquad (45)$$

Evaluating the summation indicated in (45) yields

$$f'' = 1 - (x/2) \qquad (46)$$

It is seen immediately that f'' has the correct values for the limiting cases of $x = 0$ and $x = 1$.

Discussion

The fraction of oxygen remaining in an infinitely long "head to tail" polymer after complete intramolecular condensations has been calculated to be $1/2e$ or 18.39%. This figure is identical with the fraction of halogen that can be expected to remain in a random vinyl halide polymer after treatment with zinc. This is a remarkable coincidence for there is nothing about the two problems which would suggest that they have the same answers.

For the random methyl vinyl ketone polymer, it has been seen that 31.18% of the oxygen can be expected to remain if one assumes that 1–2 and 1–3 reactions can take place with equal ease. Although it will not be proved here, it can be shown that the same answer would be obtained if 1–2 condensations took place infinitely faster than 1–3 reactions. In general the answer will depend upon the relative rates of the two kinds of condensations, unlike the situation involved in the removal of substituents.[2c] The fraction remaining, however, should not be very different from that calculated above even for the most general case. It can also be shown that if 1–2 pairs of acetyls react rapidly to form furan rings instead of structures analogous to II and III, then the same answer would be obtained again.

With regard to copolymers, it is interesting to note that f' lies approximately half way between f and f'', at least for small values of x. This is exactly true in the series expressions (40), (44), and (46) up to, but not including, the cubic terms. It is very likely that f' is nearly the mean of f and f'' over the whole range of values for x since this approximation is not bad even for $x = 1$. This behavior seems quite reasonable for the problem at hand.

Recent experiments by Marvel, Riddle and Corner[1b] have been interpreted in light of the calculations of this paper. In conclusion the author wishes to express his appreciation to Professor C. S. Marvel for his helpful discussion.

Summary

The statistical problem involved in the removal of oxygen through intramolecular aldol condensations has been carried out for infinitely long "head to tail," random, and "head to head–tail to tail" polymers. The results for pure polymers are then extended to copolymers.

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