magnesium halide with propylene oxide, by oxidation to the corresponding phenyl acetone. The same carbinol was obtained by the addition of propylene oxide to the Grignard reagent, by the addition of filtered Grignard reagent to propylene oxide,[2] and by reaction of xylyl magnesium chloride with acetaldehyde.[3] The identity of the carbinols was proved by formation of urethans that melted at the same temperature and gave no depression in mixed melts.

***p*-Xylylmethylcarbinol.**—To 38.7 g. (1.6 moles) of magnesium in a 3-liter Wolff flask fitted with mechanical stirrer, addition funnel and efficient reflux condenser are added 115 ml. of absolute ether, an iodine crystal, and 1 ml. of *p*-bromotoluene. When the reaction has begun a solution of 256.5 g. (1.5 moles) of *p*-bromotoluene in 590 ml. of ether is added with rapid stirring at a rate such that constant reflux is maintained. Thereafter the mixture is refluxed for one hour, cooled to below 10°, and 88.0 g. (1.5 moles) of propylene oxide added over a four-hour period. After refluxing for one hour longer 300 ml. of ether is distilled off, 300 ml. of benzene added and the distillation continued until the temperature of the vapor is 67°. Decomposition of the addition product is effected by the careful addition of 600 g. of an ice water slush and 30% sulfuric acid until the aqueous layer is acid to congo red. The layers are separated, the aqueous layer extracted repeatedly with ether, and the ether extracts combined and dried over anhydrous potassium carbonate. After the ether is removed the liquid is fractionated twice under reduced pressure to give 87.1 g. of carbinol, b. p. 84–85° (2 mm.), d^{25}_{25} 0.9760, n^{25}_{D} 1.5202, R_L obsd. 46.77, calcd. 46.30. The high boiling fraction which solidifies on distillation is *pp'*-ditolyl, m. p. 121°. The solid phenylurethan prepared from the carbinol melts at 111.0–111.5°.

Anal. Calcd. for $C_{17}H_{19}O_2N$: N, 5.20. Found: N, 5.24.

***m*-Xylylmethylcarbinol.**—Prepared by the same procedure from *m*-bromotoluene, this compound has the properties: b. p. 89.91° (2 mm.), d^{25}_{25} 0.9777, n^{25}_{D} 1.5201, R_L obsd. 46.68, calcd. 46.30. The phenylurethan melts at 77.5–78°.

Anal. Calcd. for $C_{17}H_{19}O_2N$: N, 5.20. Found: N, 5.26.

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(2) Kharasch and Clapp, *J. Org. Chem.*, **3**, 355 (1938).

(3) Drake and Cooke, "Organic Syntheses," Vol. XII, John Wiley and Sons, New York, N. Y., 1932, p. 48.

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Removal of Substituents from Vinyl Polymers

BY ROBERT SIMHA[1]

In a recent publication Wall[2] has considered the problem of the removal of chloride groups by zinc from polyvinyl chains containing chloride (X) and acetate (Y) substituents. From statistical considerations he obtained the distribution of a given number of X's and Y's along the linear chain. Then, using and extending the results of Flory[3] he derived an expression for the fraction of chlorides remaining after completion of the reaction with zinc. The computations were performed for the case of 1–3 polymers, as well as for random ones, that is, for vinyl units oriented at random. The main assumption made thereby is that a reaction of a substituent with another one farther removed than the next substituent, can be disregarded, and that 1–4 pairs cannot be removed together.

Wall finds for the number p_i of groups of X's in one polyvinyl chain containing i members the expression

$$p_i = (n_X + n_Y)x^i(1 - x)^2 \qquad (1)$$

where

$$x = \frac{n_X}{n_X + n_Y} = \frac{n_X}{n}$$

the fractional number of chlorides in a chain. n_X denotes the average number of chlorides contained in one chain and n_Y is the corresponding quantity for the acetates.

Several years ago Kuhn[4] considered the size distribution of degradation products generated by the random splitting of long chain molecules. His result, although obtained by a somewhat different method, is identical with Wall's if $1 - x$ denotes the average fraction of bonds cut per original molecule divided by the initial number of linkages per chain.

This is to be expected as the problem is the same, namely, the distribution of two species (splitting and conservation of bonds) over a given number of places. However, Kuhn's treatment is only approximately valid. Equation (1) holds for the case of an infinitely long chain when the end products or the groups of X's are much smaller than the whole chain, as stated by both authors.

This point has been considered recently by Montroll and the author[5] for the depolymerization problem. The same reasoning also applies to the present question. The treatment used here differs

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(1) Lalor Foundation Fellow, 1940–1941.

(2) Frederick T. Wall, THIS JOURNAL, **62**, 803 (1940).

(3) Paul J. Flory, *ibid.*, **61**, 1518 (1939).

(4) W. Kuhn, *Ber.*, **63**, 1503 (1930).

(5) Elliott W. Montroll and Robert Simha, *J. Chem. Phys.*, **8**, 721 (1940). The same results can be obtained directly from the general rate equations for a depolymerization reaction or similar processes. This method allows also a treatment of the distribution due to non-random splitting (R. Simha, in preparation).

from the previous ones and involves two steps:

(a) A consideration of the arrangement of X's along one single chain in terms of the total number of X's (or Y's) in this chain. This leads to an expression analogous to formula (2) in ref. 5, already previously derived by Durfee and Kertesz[6] and Mark and Simha.[7]

(b) A calculation of the distribution of the total number N_Y of Y's available among N different chains.

To arrive at the final result we start in the following way. Assuming that in a chain with n places available for substitution there are distributed any number n_Y' of Y's, we compute the number of times i X's follow each other without interruption. Then we consider that altogether N_Y Y's are to be distributed among N chains with n structural units. In this way we find the number of ways one particular chain can get n_Y' Y's. In order to calculate P_i, the total number of chlorides embodied in groups of i members, we must remember that a chain can have 1,2 . . . $n - i$ Y's while containing i X's in succession. Summing over all these possibilities, and introducing $x = N_X/Nn = n_X/n$ the average fraction of X's per unit, we derive in analogy to equation (8) of ref. (5)

$$\left.\begin{aligned} P_i &= N(1-x)x^i[2 + (n-i-1)(1-x)];\ i \leqq n-1 \\ P_n &= Nx^n \end{aligned}\right\} \quad (1a)$$

(1a) is valid for any value of n, and involves only the trivial assumption N_X, $N_Y \gg n$. The quantity multiplied by the factor 2 represents the effects of the ends of the chain. From the equations derived in the appendix of ref. 5 it follows that

$$\sum_{i=0}^{n} iP_i = Nn_X = N_X$$

In case the initial material is not homogeneous, but consists of a certain number of fractions or can be represented by a smooth distribution curve, equation (1a) becomes a sum or an integral over all the values of $n \geqq i$, and x is correspondingly modified.

If $(n - 1)(1 - x) \gg i(1 - x) - 2$, *i. e.*, for large values of n and small values of x, (1a) reduces to (1), if $N = 1$.

Wall then proceeds to a calculation of the fraction f of chlorides becoming isolated in the polymer after reduction. If S_i is the average number of unreacted X's in a group originally containing i members, then

$$f = \frac{1}{N_X}\sum_{i=0}^{n} S_iP_i = \frac{N}{N_X}\sum_{i=0}^{n-1} S_ix^i[2(1-x) + (n-i-1)(1-x)^2] + \frac{N}{N_X}S_nx^n$$

or considering the lower and upper limits of the sums

$$f = \frac{1}{n}\sum_{i=0}^{n-1} x^i(n-i)(\Delta_{i+1} - \Delta_i)$$

with $\Delta_i = S_i - S_{i-1}$, following Flory's and Wall's notation.

If the substituents are 1–3 with respect to each other, we find, using Flory's result for Δ_i

$$f = \frac{1}{n}\sum_{i=0}^{n-1} x^i(n-i)\frac{(-2)^i}{i!} \quad (2a)$$

For $x = 1$ this reduces to Flory's value for finite chain lengths. For smaller values of $n (n < 10)$, f is found by direct evaluation of the sum. In the practically more important case of long chains it is better to use the representation

$$f = \left[e^{-2x} - \sum_{k=n}^{\infty}\frac{(-2x)^k}{k!}\right]\left(1 + \frac{2x}{n}\right) + \frac{(-2x)^n}{n!} \quad (2a')$$

For $n \longrightarrow \infty$, this reduces to Wall's equation, $f = e^{-2x}$. For large values of n the correction term is $(2x/n)e^{-2x}$, expressing the influence of substituents at the ends of the polyvinyl chain. The relative amount of unreacted X's is larger as compared with the case of an infinite chain.

If the substituents are coupled at random along the chain, the final result becomes, applying Wall's expression for Δ_i

$$f = \frac{1}{2n}\sum_{i=0}^{n-1}(-1)^i\frac{(n-i)(i+2)}{i!}x^i \quad (2b)$$

or

$$f = \left[e^{-x} - \sum_{k=n}^{\infty}\frac{(-x)^k}{k!}\right]\left[1 - x\frac{(n-3+x)}{2n}\right] + \frac{(-x)^n}{n!}\left(1 - \frac{x}{2}\right) \quad (2b')$$

Again for $n \longrightarrow \infty$, we get Wall's formula $f = e^{-x}\left(1 - \frac{x}{2}\right)$. If n is large, the dominant correction term is $e^{-x}\frac{(3-x)x}{2n}$.

In the last issue of THIS JOURNAL, Wall[8] considers a third case, namely that of "head to head–tail to tail" units following each other alternately. Then $S_i = 1$, $i \neq 0$, and

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(6) W. H. Durfee and Z. I. Kertesz, THIS JOURNAL, **62**, 1196 (1940).

(7) H. Mark and R. Simha, *Trans. Faraday Soc.*, **36**, 611 (1940).

(8) Frederick T. Wall, THIS JOURNAL, **63**, 821 (1941).

$$= \frac{N}{N_x} \sum_{i=1}^{n-1} x^i(1 - x)[2 + (n - i - 1)(1 - x)] + \frac{N}{N_x} x^n = 1 - x + \frac{x}{n} \quad (2c)$$

as found from the equations derived in the appendix of Ref. 5. The correction term for finite n and x is simply x/n.

By preparing different samples of the copolymer having different molecular weights, and different chlorine contents, it should be possible to test these considerations and the assumptions involved. It may be noted that (2b) was derived by assuming that the reaction rates for 1–2 and 1–3 pairs are equal, and reactions between 1–4 substituents do not occur. The condition that 1–2 reactions proceed much more rapidly or much more slowly than 1–3 reactions, does not alter the result. This was shown by Flory. Wall[8] proved this to be true for any value of the relative rate of reaction of 1–2 and 1–3 pairs.

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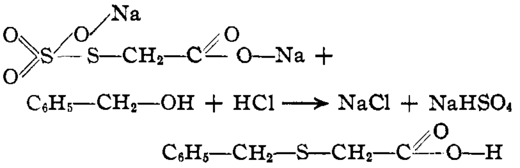
Preparation of S-Benzylmercaptoacetic Acid

BY GEORGE G. STONER AND GREGG DOUGHERTY

Certain alcohols can be condensed readily with mercaptans to yield sulfides. For example S-benzylmercaptoacetic acid was isolated in 72% yield after equimolar quantities of benzyl alcohol and mercaptoacetic acid had reacted in 2 N hydrochloric acid.[1] It has now been found that the same end can be achieved more directly and conveniently by using the Bunte salt, disodium S-carboxymethyl thiosulfate, prepared from chloroacetic acid and sodium thiosulfate.



(1)

Experimental Part

Solution of S-Carboxymethyl Thiosulfuric Acid.—Chloroacetic acid (9.5 g., 0.1 mole) was neutralized by sodium carbonate in 25 cc. of water, a solution of 25 g. (0.1 mole) of sodium thiosulfate in 40 cc. of water was added, and the resulting solution was kept at 100° for an hour. After cooling, 50 cc. (0.6 mole) of concentrated hydrochloric acid was added. No sulfur precipitated, but about 1 g. of sodium chloride was filtered off.

S-Benzylmercaptoacetic Acid.—The above solution was refluxed for twenty hours with 10.8 g. (0.1 mole) of benzyl alcohol. The oily layer was neutralized by sodium carbonate solution and washed with ether. Then 9.1 cc. (0.11 mole) of concentrated hydrochloric acid was added and after standing one day at 5° a yield of 10 g. (55%) was obtained, m. p. 60–61°,[2] equivalent weight calcd. 182.2, found 183.

Racemic Benzylsulfinylacetic Acid.—To a solution of 0.91 g. (0.005 mole) of S-benzylmercaptoacetic acid in 40 cc. of acetone, 0.55 cc. (0.0055 mole) of 30% hydrogen peroxide was added. The beaker was left uncovered for five days, by which time the solvent had evaporated, leaving a quantitative yield of sulfoxide, m. p. 126–127° after recrystallization from benzene.

Anal. Calcd. for $C_9H_{10}O_3S$: equiv. wt., 198.2; S, 16.17. Found: equiv. wt., 201; S, 16.5.

Benzylsulfonylacetic Acid.—A solution of 0.91 g. (0.005 mole) of S-benzylmercaptoacetic acid in 10 cc. of water was oxidized at room temperature for five days by 32 cc. (20% excess) of 4% potassium permanganate solution. The mixture was filtered and 0.05 mole of sulfuric acid was added. The solution was shaken with three 50 cc. portions of ether, 100 cc. of benzene was added to the extract, which then was concentrated to 40 cc. After one hour, 0.65 g. (60% yield) of fine crystals formed, m. p. 137°.[3]

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[1] Holmberg, *J. prakt. Chem.*, **141**, 93 (1934).

[2] Berg and Holmberg, *Svensk Kem. Tids.*, **47**, 257 (1935), reported 60°; Holmberg, *loc. cit.*, and *Arkiv Kemi, Mineral. Geol.*, **12A**, No. 11 (1936), reported 61–63°.

[3] Rothstein, *J. Chem. Soc.*, 309 (1937), reported 139–140°.

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The Use of Sulfuric Acid in Purifying Saturated Hydrocarbons: Its Action on 2,2,4-Trimethylpentane

BY FRANK C. WHITMORE AND H. H. JOHNSON, JR.

The use of sulfuric acid as a wash in the purification of saturated hydrocarbons is widespread. Observation has long led us in this Laboratory to the suspicion that such treatment is questionable. We have now studied the action of cold concentrated sulfuric acid on 2,2,4-trimethylpentane, isooctane. After treatment for ten days with cold 95% acid, we find that over half of the starting material has been changed to other products. Although the nature of these products has not been determined, there is no doubt that sulfuric acid has brought about profound changes.

The extent to which reaction took place makes imperative a most careful fractionation of a saturated hydrocarbon following a sulfuric acid wash. This fact and the possible loss of expensive material raise a real question as to the desirability of this method of purification.