The compounds were added to the test solution (0.1 g. of luminol dissolved in 100 ml. of 5% sodium carbonate solution, to which was then added 20 ml. of 3% hydrogen peroxide) in the form of aqueous solutions of their sodium salts. The iron complex salts thus naturally were present in the *alkaline* solution as "hematins," the halogen atom having been replaced by hydroxyl.

Iron bacteriochlorin e_6 trimethyl ester (bacteriochlorin e_6 trimethyl ester-hemin) which is not reported in the literature so far, was prepared by the following method: bacteriochlorin e_6 trimethyl ester derived from bacteriochlorophyll[3] was treated in the usual way (under nitrogen, for half an hour on a steam-bath) with a freshly prepared ferrous acetate–sodium chloride solution in glacial acetic acid.[4] The reaction mixture was poured into chloroform and the chloroform solution was washed free of acetic acid and excess iron. It was then evaporated to dryness, the residue was dissolved in hot glacial acetic acid containing a little sodium chloride, and the solution was filtered. On standing the bacteriochlorin e_6 trimethyl ester-hemin crystallized.

Absorption Spectra.—In pyridine–ether or in chloroform: three maxima at 695, about 596, 543.5 μμ and an end absorption at the blue end of the spectrum. The first maximum of absorption is very intense, the second one very weak (in pyridine–ether almost invisible). Sequence of intensities: I; III, II. In glacial acetic acid–ether (1 + 1): 686, 623 μμ. II, I. The solutions do not fluoresce.

A solution of a sodium salt of bacteriochlorin e_6-hemin, as used in the chemiluminescence test, was obtained by shaking the ester at room temperature with 1 *N* sodium hydroxide in methanol. This brought enough sodium salt (mono-, di-, or tri-sodium salt ?) of bacteriochlorin e_6-hemin in solution. The solution was prepared freshly each time for the luminescence test, as side reactions (dehydrogenation ?) occur on standing. It is not possible to saponify the ester by refluxing it in alcoholic sodium hydroxide, as the complexly bound iron is partly eliminated and other side reactions take place.

Chlorin e_6-hemin was prepared from chlorin e_6 with ferrous acetate–sodium chloride in glacial acetic acid and worked up over chloroform as described above. (The yield of crystalline material is very poor.) The absorption spectrum is identical with that of the chlorin e_6 trimethyl ester-hemin given by Fischer and Wunderer[5] the main absorption maximum being at 619 μμ (chloroform solution).

From what was known it was to be expected that those substances free of complexly bound metal (pheophorbide, chlorin e_6, deuteroporphyrin, coproporphyrin) would have no catalytic effect. Furthermore, in view of the fact that Cook[1] found a weak catalytic action of a number of metal phthalocyanines other than iron phthalocyanine, it is not surprising that sulfonated copper phthalocyanine and copper deuteroporphyrin also exhibit such weak catalytic properties. However, a catalytic effect as strong as that of hemin could not have been postulated from iron complexes of such chlorophyll derivatives which are not porphyrins but have the phorbine structure[6] (dihydroporphin structure with cyclopentanone ring) as iron pheophorbide, or have the chlorin structure (dihydroporphin structure) as iron chlorin e_6, or even have the dihydrochlorin structure (tetrahydroporphin structure) as iron bacteriochlorin e_6. With these results in mind, the weak catalytic effects of chlorophyllin (magnesium complex) and copper chlorin e_6 only complete the picture.

The iron complexes of chlorophyll derivatives which were found to have a strong catalytic action have the coördinative association of the iron atoms with four pyrrole nitrogen atoms as found in hemin or iron phthalocyanine, which configuration obviously is sufficient to make the substance potentially catalytically active, other structural factors (side chains, cyclopentanone ring, degree of saturation, di- and tetrahydroporphin structure) having no influence.

Chemiluminescence also has been observed by Helberger and Hevér[7] and by Rothemund[8] when metal complexes of porphyrins were heated with organic solvents containing peroxides. However, whereas these authors report no or a very weak effect of iron and copper complexes of porphyrins and a strong catalytic action of magnesium (and zinc) complexes, the chemiluminescence (peroxide decomposition) of luminol is very strongly catalyzed by iron complexes and only very little by the magnesium complex chloroprophyllin. Furthermore, whereas the luminescence observed by Helberger and Hevér and by Rothemund goes on simultaneously with a rapid decomposition of the catalysts, the iron chlorophyll derivatives catalyzing the luminescence of luminol are destroyed so slowly that it is hard to observe their decomposition.

---

[3] H. Fischer, R. Lambrecht and H. Mittenzwei, *Z. physiol. Chem.*, **253**, 38 (1938).

[4] H. Fischer and H. Orth, "Die Chemie des Pyrrols," Vol. 2, II, **1940**, p. 332.

[5] H. Fischer and A. Wunderer, *Ann.*, **533**, 241 (1938).

[6] H. Fischer and H. Orth, ref. 4, Vol. 2, II, 1940, p. 41.

[7] J. H. Helberger and D. B. Hevér, *Ber.*, **72B**, 11 (1939).

[8] P. Rothemund, THIS JOURNAL, **60**, 2005 (1938).

JOVAN LABORATORIES, INC.
NEW YORK, N. Y.

RECEIVED MARCH 7, 1941

Xylyl Methyl Carbinols

BY J. G. SHAREFKIN AND J. J. RITTER

Levene[1] proved the structures of secondary alcohols, obtained from the reaction of phenyl-

---

[1] Levene and Walti, *J. Biol. Chem.*, **90**, 86 (1931).

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.

---

(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.

BROOKLYN COLLEGE
NEW YORK UNIVERSITY
NEW YORK CITY

RECEIVED FEBRUARY 1, 1941

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

$$p_i = (n_{\mathrm{X}} + n_{\mathrm{Y}})x^i(1 - x)^2 \qquad (1)$$

where

$$x = \frac{n_{\mathrm{X}}}{n_{\mathrm{X}} + n_{\mathrm{Y}}} = \frac{n_{\mathrm{X}}}{n}$$

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

---

[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).