able. Assuming, however, that with 0.002 N oxalic acid, for periods up to five hours, there is no conversion of chlorophyll *b*, we have recalculated some values on the basis of a 25% inert ingredient, *i. e.*, the chlorophyll *b*. Under these conditions, the oxalic results fall in line with the others, and we are given little preference between k_1 and k_2 for chlorophyll.

A limitation must be remembered, that with the visual B and L spectrophotometer, we cannot vary our chlorophyll concentrations within a wider range than 3 to 5 times without loss of accuracy. Initial concentrations of chlorophyll in the present experiments were 0.5×10^{-4} M, and the acid varied from 0.01 to 0.002 N for chlorophyll *a* and from 0.10 to 0.01 N for chlorophyll *b*.

The present values show no falling off with time, indicating there may be an error inherent in our earlier calculations as there could be no accurate compensation for the effect of chlorophyll *b*. The k_1/N values are in both cases more constant than those for k_2/N, and in two of the acid levels for chlorophyll *b*, and in three for *a*, the deviations are smaller for k_1 than for k_2. Furthermore, there is very little trend in the k_1 values, while in some cases there is a definite upward trend for k_2. We are therefore inclined to believe that the reaction is of first order with respect to both chlorophyll components.

An explanation is required for the fact that with 0.01 N oxalic acid, k_1/N for chlorophyll *a* has a value of 139, for chlorophyll *b*, 14.8. If the reactions are correctly interpreted on the basis of first order in both cases, the question arises as to the cause of this difference. We hope to throw further light on this in studies on the removal of magnesium from allomerized components, phytol-free derivatives, and the heats of activation.

Conclusions.—For the pure *a* and *b* chlorophyll components, it is confirmed that the reaction involving loss of magnesium is of first order with respect to acid. It is probably of the same order with respect to chlorophyll. The two hydrogens replacing the magnesium must therefore enter at different rates, and in all probability the entrance of the first hydrogen is the rate-governing step. This would materially weaken the remaining magnesium–nitrogen bond, in which respect it would then no longer be equivalent to the initial condition, presumably highly covalent in character.

The chlorophyll *a* reacts from seven to nine times more rapidly than chlorophyll *b*.

FRUIT PRODUCTS DIVISION
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA
RECEIVED OCTOBER 13, 1939

The Synthesis of Amino Acids from Benzoylaminomalonic Ester

BY E. P. PAINTER

The use of benzoylaminodiethyl malonate in the synthesis of amino acids as recently reported by Redemann and Dunn[1] has been found to be superior in many respects to the malonic ester and phthalimido malonic ester methods.[2]

The ester alkylates in absolute alcohol with all alkyl halides tried. The ester or derivatives is readily hydrolyzed with constant boiling hydrochloric or hydrobromic acid. Glycine can be isolated in 85% yields by hydrolyzing the free ester with concentrated hydrobromic acid. To the list of amino acids prepared in good yields by Redemann and Dunn by the use of this reagent may be added norleucine, α-amino-γ-phenoxy-*n*-butyric acid and the lactone of α-amino-γ-hydroxy-*n*-butyric acid. These have been isolated after hydrolysis of the ester alkylated with *n*-butyl bromide, β-bromoethyl phenyl ether and ethylene bromohydrin.

In an attempt to prepare β- and γ-halogen amino acids benzoylaminomalonic ester has been alkylated with methylene dibromide, ethylene bromide and ethylene chloride. The products formed contain some halogen but always less than the theoretical amount and the desired amino acids have not been isolated after hydrolysis.

The aminomalonic ester was prepared by the method of Cerchez,[3] excepting the reduction was carried out in alkaline solution with aluminum amalgam made from aluminum turnings and the amino ester benzoylated in a suspension of sodium carbonate in ether saturated with water. By carrying the reaction straight through to the benzoyl compound without isolating the intermediary products, 40–45% over-all yields may be expected. Redemann and Dunn were able to obtain slightly better yields of benzoylaminomalonic ester, but their procedure is more expensive and not as convenient for many laboratories.

The use of anhydrous reagents in alkylations should be emphasized.

(1) Redemann and Dunn, *J. Biol. Chem.*, **130**, 341–348 (1939).

(2) Painter, Ph.D. Thesis, U. of Minnesota, 1939.

(3) Cerchez, *Bull. soc. chim.*. [4] **47**, 1281 (1930).

From the author's experience and the paper by Redemann and Dunn it appears that benzoylaminomalonic ester should find general use in the synthesis of α-amino acids.

DIVISION OF AGRICULTURAL BIOCHEMISTRY
COLLEGE OF AGRICULTURE
UNIVERSITY OF MINNESOTA
ST. PAUL, MINNESOTA
RECEIVED NOVEMBER 15, 1939

The 3-Nitrophthalates of the Mono Ethers of Ethylene and Diethylene Glycol

BY A. J. VERAGUTH[1] AND HARVEY DIEHL

The problem of identifying the monoethyl ether of ethylene glycol (Cellosolve) arose here recently and was successfully solved by the use of the 3-nitrophthalic anhydride reagent proposed by Nicolet and Sachs[2] for the identification of alcohols. The work has now been extended to the other commercially available monoethers of ethylene glycol ("Cellosolve" series), and of diethylene glycol ("Carbitol" series).

The ethers were obtained from the Carbide and Carbon Chemicals Corporation, and were purified by fractional distillation. A constant boiling fraction was taken, the boiling points and refractive indices checking with recorded values.

The procedure followed for the preparation of the acid 3-nitrophthalate esters of these ether alcohols was essentially that recommended by Nicolet and Sachs.

The anhydride was heated with an excess of the ether alcohol at the boiling point of the latter until all of the anhydride had dissolved and then for fifteen minutes longer. In the cases of those liquids having boiling points above 150°, toluene was added to avoid higher temperatures which cause decomposition of the esters formed; the toluene was then removed by distillation under reduced pressure. The oily layer of ester was then extracted with hot water to remove the unreacted reagents. It was then treated with a hot mixture of water and the least amount of ethyl alcohol necessary to effect complete solution. This solution was allowed to cool slowly with frequent scratching to induce crystallization. The initial crystallization was generally very slow, periods of standing for several days in a refrigerator sometimes being required. Recrystallization was continued until a constant melting point was obtained, generally three to five recrystallizations. Toluene was found to be a better solvent for recrystallization of the monophenyl ether of ethylene glycol than the water–alcohol mixtures.

Molecular weights of the derivatives were determined by titrating, with standard alkali, a solution containing 0.5 g. of the ester in 50% alcohol, using phenolphthalein as indicator. The melting points were taken with standard Anschütz thermometers in a mechanically stirred bath.

White crystalline derivatives were obtained from the monomethyl, monoethyl, monobutyl and monophenyl ethers of ethylene glycol and from the monomethyl ether of diethylene glycol but not from the monobenzyl ether of ethylene glycol or from the monoethyl or monobutyl ethers of diethylene glycol.

The 3-nitrophthalates obtained from the monoethyl ether of ethylene glycol and from the monomethyl ether of diethylene glycol crystallize with one molecule of water. Their water of crystallization was determined by drying a weighed amount of the ester in a vacuum at 100° over anhydrous magnesium perchlorate (Fischer drying pistol). The percentages of water found were 5.89 and 5.83, the calculated values being 5.98 and 5.43, respectively.

TABLE I

3-NITROPHTHALATES OF MONO ALKYL ETHERS OF ETHYLENE GLYCOL

Alkyl	3-Nitrophalates M. P., °C.	Mol. wt. Calcd.	Mol. wt. Found
Methyl	128.4–129.0	269	268 ± 1
Ethyl	118.0–118.6	283	284 ± 3
Ethyl (monohydrate)	94.2–94.5	301	302 ± 4
Butyl	121.0–120.6	311	311 ± 1
Phenyl	112.0–113.0	331	330 ± 2

The 3-nitrophthalate monohydrate of the monomethyl ether of diethylene glycol was also a white crystalline solid and melted at 87–90°. The anhydrous 3-nitrophthalate melted at 91.4–92.2° and was found to have a molecular weight of 313 ± 1, as compared with the calculated value of 313. All attempts to induce the liquid reaction products from the monobenzyl ether of ethylene glycol ("Benzyl Cellosolve") and the monoethyl and monobutyl ethers of diethylene glycol ("Carbitol" and "Butyl Carbitol," respectively) to crystallize failed.

DEPARTMENT OF CHEMISTRY
PURDUE UNIVERSITY
LAFAYETTE, INDIANA
RECEIVED OCTOBER 9, 1939

---

(1) Taken from a Thesis submitted to the Faculty of Purdue University by Mr. Veraguth in partial fulfilment of the requirements for the Degree of Master of Science.

(2) Nicolet and Sachs, THIS JOURNAL, **47**, 2348 (1925); see also the further work of Dickinson, Crosson and Copenhaver, *ibid.*, **59**, 1094 (1937).