[CONTRIBUTION FROM THE NORTHERN REGIONAL RESEARCH LABORATORY[1]]

Polysaccharide Aryl Carbamates. II. Nuclear Substituted Tricarbanilates of Corn Starch, Corn Amylose and Amylopectin

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Trisubstituted *o*- and *m*-chlorocarbanilates, 2,5-dichlorocarbanilates, *o*-, *m*- and *p*-methylcarbanilates, and *p*-bromocarbanilates of corn starch, corn amylose and amylopectin were prepared by reaction of the polysaccharide with the appropriate isocyanate in pyridine. At 80° the order of reactivity of the various aryl isocyanates with corn starch granules was *m*-chlorophenyl > phenyl > *m*-tolyl > 2,5-dichlorophenyl > *o*-chlorophenyl > *p*-bromophenyl > *p*-tolyl > *o*-tolyl > α-naphthyl. A chelate structure for the *o*-chloro- and *o*-methylcarbanilates has been proposed. In conformity with the postulated intramolecular bonding, these ortho-substituted derivatives have greatly different optical rotations, lower melting ranges and, for the chloro compounds, lower solution viscosity and increased solubility in non-polar organic solvents as compared with the meta and para isomers.

In a previous publication[2] we have described the reaction of a number of amylaceous polysaccharides with phenyl and α-naphthyl isocyanates. The triesters were readily prepared, and their optical rotations in pyridine were found to be correlated with the structures of the polysaccharide raw materials.

This work has now been extended to a study of the condensation of several nuclear-substituted phenyl isocyanates with corn starch and its component fractions, amylose and amylopectin. The relative rates of reaction of these reagents with starch, and the solubilities, melting ranges, and optical rotations of the various compounds have been determined. A pronounced "ortho effect" was found which modified the properties of the ortho-substituted derivatives as compared with the meta and para isomers.

The effect of temperature on the rate of reaction of phenyl isocyanate with corn starch granules (using twice the amount of reagent theoretically needed for trisubstitution) is shown in Fig. 1. The intermediate temperature was selected for comparing the reaction rates of the various isocyanates. At this temperature (Fig. 2) substantial differences in the reactivity of starch with the substituted isocyanates were demonstrated. In each group of isomeric isocyanates the ortho compound reacted most slowly, due possibly to steric effects. The order of reactivity of these isocyanate reagents with corn starch granules is not the same as that found for partially acetylated cellulose.[3] This may be attributable to the greater heterogeneity of our reaction mixture, in which the reagent had to effect disorganization of the starch granule as well as its subsequent esterification.

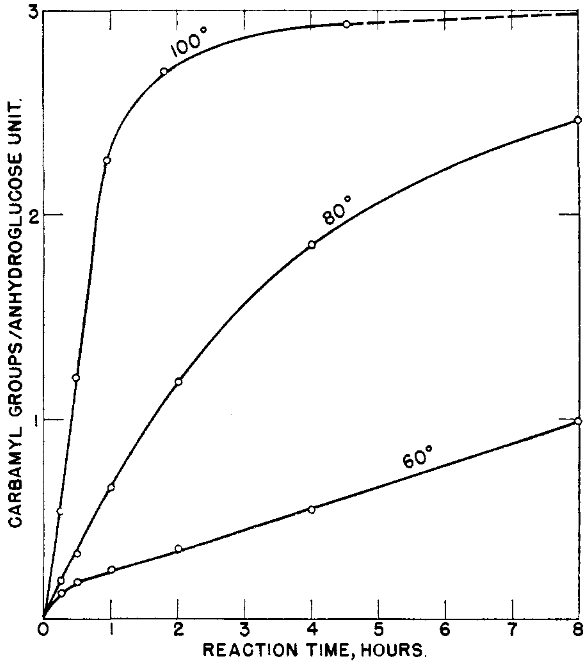

Fig. 1.—The effect of temperature on the rate of reaction of phenyl isocyanate with corn starch granules.

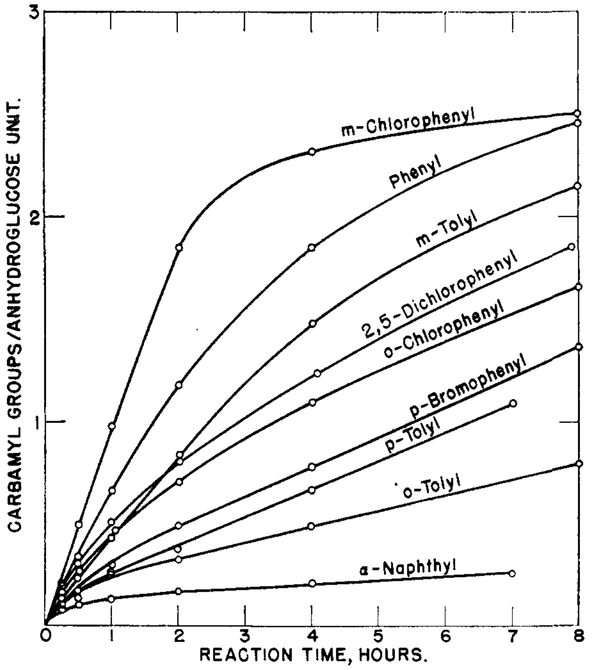

Fig. 2.—Rate of reaction of various isocyanates with corn starch at 80°.

With all of the reagents trisubstitution of corn starch, corn amylose and amylopectin could easily be achieved in a reaction time of 24 hours at 100°. The optical rotations and melting ranges of these completely substituted esters are given in Table I.

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[1] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

[2] I. A. Wolff and C. E. Rist, THIS JOURNAL, **70**, 2779 (1948).

[3] W. M. Hearon and J. L. Lobsitz, *ibid.*, **70**, 296 (1948).

TABLE I

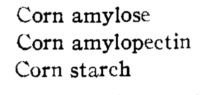
PROPERTIES OF THE TRISUBSTITUTED CARBANILATES

Compound	$[\alpha]^{25}D$ (c 1)		Melting range, °C.[b]	Analyses, %, dry basis			
				Nitrogen		Halogen	
	Pyridine	Morpholine		Calcd.	Found	Calcd.	Found
o-Chlorocarbanilates							
Corn amylose	− 24°	+ 30°	180–210	6.75	6.87	17.1	17.1
Corn amylopectin	− 19	+ 37	170–200	6.75	6.90	17.1	17.4
Corn starch	− 20	[a]	190–205	6.75	6.81	17.1	17.3
m-Chlorocarbanilates							
Corn amylose	−190	− 41	265–275	6.75	6.76	17.1	17.1
Corn amylopectin	−130	− 27	250–270	6.75	6.69	17.1	17.0
Corn starch	−147	[a]	260–280	6.75	6.67	17.1	17.1
2,5-Dichlorocarbanilates							
Corn amylose	− 42	[a]	190–220	5.79	5.84	29.3	29.4
Corn amylopectin	− 33	[a]	185–215	5.79	5.88	29.3	29.6
Corn starch	− 34	[a]	185–215	5.79	5.91	29.3	29.5
o-Methylcarbanilates							
Corn amylose	− 8	+ 38	235–260	7.49	7.49		
Corn amylopectin	− 3	+ 40	225–245	7.49	7.44		
Corn starch	− 4	[a]	230–250	7.49	7.29		
m-Methylcarbanilates							
Corn amylose	−136	− 17	265–285	7.49	7.22		
Corn amylopectin	−108	[a]	250–270	7.49	7.36		
Corn starch	−119	[a]	260–285	7.49	7.30		
p Methylcarbanilates							
Corn amylose	−107	− 37	260–280	7.49	7.44		
Corn amylopectin	− 83	[a]	255–280	7.49	7.42		
Corn starch	− 90	[a]	260–280	7.49	7.44		
p-Bromocarbanilates							
Corn amylose	−140	−109	250–270	5.56	5.40	31.75	31.9
Corn amylopectin	−118	− 84	250–270	5.56	5.63	31.75	32.2
Corn starch	−122	− 89	250–270	5.56	5.51	31.75	31.9

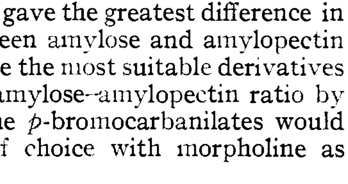
[a] Turbidity of the solution prevented determination of its rotation. The blending procedure (see Experimental) could not be used since decomposition of the ester occurred when an aliquot was evaporated to dryness for determination of the concentration. [b] Taken in capillary tubes.

As in the case of the unsubstituted tricarbanilates of starch and its fractions,[2] the optical rotations in pyridine were all negative. The *m*-chlorocarbanilates in pyridine gave the greatest difference in optical rotation between amylose and amylopectin and would therefore be the most suitable derivatives for determining the amylose–amylopectin ratio by optical rotation. The *p*-bromocarbanilates would be the derivatives of choice with morpholine as solvent.

Striking differences are apparent between the ortho-substituted derivatives and their meta or para isomers. The ortho-substituted carbanilates have lower melting ranges, considerably lower negative rotations in pyridine, and show a reversal in sign to positive optical rotation in morpholine. This "ortho effect" we attribute to a chelate structure in the ortho compounds, which can be represented by formulas I and II although it is recognized that other alternative molecular forms or configurations could be postulated.



I



II

Chlorine has been said to show little tendency to form hydrogen bonds,[4] and there are but few instances of C–H–N bridges involving the hydrogen atoms attached to a methyl group.[5] Also, known instances of chelation usually involve a six-membered ring; in fact, five-membered rings are considered somewhat less probable[5,6] or at best weakly chelated.[7] Yet *o*-chlorophenol which contains both a five-membered ring, and chlorine as the donor atom has been shown by spectroscopic evidence to form weak intramolecular hydrogen bonds.[8] The occurrence of intramolecular hydrogen bonds in *o*-

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(4) A. X. Schmidt and C. A. Marlies, "Principles of High-Polymer Theory and Practice," McGraw-Hill Book Co., Inc., New York, N. Y., 1948, pp. 33-36.

(5) L. Hunter, *Chemistry and Industry*, **60**, 32 (1941); **63**, 155 (1944).

(6) H. Gilman, Editor-in-Chief, "Organic Chemistry, An Advanced Treatise," John Wiley and Sons, Inc., New York, N. Y., 1938, p. 1643.

(7) A. E. Remick, "Electronic Interpretations of Organic Chemistry," 2nd. ed., John Wiley and Sons, Inc., New York, N. Y., 1949, p. 31.

(8) L. C. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940, p. 323.

chlorophenol is also suggested by its viscosity[9] which is considerably lower than that of the meta and para isomers. Even if the individual C–H–N and Cl–H–N attractions in our polysaccharide derivatives are fairly weak, intensification of the effect might be expected from the large number of such groupings per molecule. This then would account for the relatively large observed differences between the ortho compounds and their meta and para isomers. Barker, Hunter and Reynolds,[10] working with the *o*-chloro- and *o*-methylcarbanilates of lower aliphatic alcohols prefer to explain the lack of association of their ortho-substituted derivatives in cryoscopic molecular weight determination as due to steric factors rather than to chelation.

The solubilities of these substituted carbanilates in organic solvents were generally similar to those reported for the unsubstituted derivatives,[2] with a single exception. The tri-*o*-chlorocarbanilates, in addition to showing good solubility in pyridine, morpholine, dioxane and ethyl acetate, were completely soluble in chloroform and benzene. This solubility in the latter two solvents distinguishes the derivatives from all other polysaccharide carbanilates thus far prepared and is consistent with their postulated chelate structure. The intramolecular bonding must be weaker in the *o*-methyl than in the *o*-chloro derivative, since increased solubility of the former in non-polar organic solvents was not observed. Further evidence for the weakness of the C–H–N bond (structure II) is the fact (Table I) that the lowering of the melting range of the ortho from that of the meta and para isomers was less in the tolyl than in the chlorophenyl series. The 2,5-dichlorocarbanilates, containing both the ortho and meta substituents have properties similar to those of the *o*-chlorocarbanilates indicating their chelate structure. The starch and amylopectin dichlorocarbanilates were less readily soluble than the amylose derivative.

Finally, the intramolecular satisfaction of secondary valence forces in the *o*-chloro derivatives and lack thereof in the *m*-chloro compounds was shown by the differences in their solution viscosities. Solutions (0.5% concentration) of these two amylose esters in pyridine had, at 25°, viscosities of 1.37 and 4.47 centipoises, respectively. In the meta compound, association between molecules is indicated by the higher viscosity value.

Experimental

Materials.—The corn starch and its fractions were obtained as previously described.[2] *p*-Bromophenyl isocyanate was Eastman Kodak Company Practical grade. Since the melting point (39–41°) checked that reported in the literature, the product was used without further purification. The other isocyanates, Eastman Kodak Company white label chemicals, were purified by vacuum distillation prior to use when discoloration or the presence of a precipitate was noted.

Rate of Reaction Studies.—The following procedure was used in all of the rate studies. Ten grams (air-dry weight) of corn starch was dried azeotropically with pyridine by distilling 100 ml. through a 6-inch Vigreux column. The dry starch in 150 ml. of pyridine was allowed to stand overnight. Twice the quantity of isocyanate theoretically needed for trisubstitution was then added all at once, and the flask was immediately surrounded by an oil-bath, maintained at the desired temperature ±0.5°. Mechanical stirring was maintained throughout the course of the reaction. Samples were withdrawn after the time intervals indicated by points on Figs. 1 and 2, and immediately blended with absolute ethanol to halt reaction and precipitate the ester. The samples were washed thrice more with ethanol, dried and analyzed for nitrogen by the Kjeldahl procedure. Sample calculation of the degree of substitution from the nitrogen analysis for an unsubstituted carbanilate is

$$\frac{1400x}{162 + 119x} = \%\ \text{nitrogen (dry basis)}$$

where x represents the degree of substitution per anhydroglucose unit.

Preparation of the Triesters.—Five grams of the polysaccharide was esterified and the product isolated as in the rate studies described above. A uniform reaction time of 24 hours at 100° and a twofold excess of reagent were used. Nitrogen and halogen analyses on the triesters agreed closely with the values calculated for completely substituted products.

Optical Rotations.—Optical rotations were taken as previously described.[2] Discoloration of the ester and failure to achieve constant weight occurred when an aliquot of the morpholine solution of certain of the carbanilates (indicated in Table I) was evaporated to dryness for determination of concentration. Rotations are not reported on these materials.

Viscosities.—Solutions were prepared for viscosity determination by weighing 0.2500 g. (dry basis) of amylose tri-*o*- and *m*-chlorocarbanilates into 50-ml. volumetric flasks and taking the esters into solution in pyridine. Viscosities were taken in Ostwald–Cannon–Fenske capillary type viscometers held in a thermostatically-controlled water-bath at 25.10 ± 0.03°. Kinetic energy corrections were applied.

The use of trade names in this paper does not necessarily constitute endorsement of these products nor of manufacturers thereof.

Acknowledgment.—We are indebted to Mrs. Mary B. Wiele for carrying out nitrogen and halogen analyses on the compounds reported in this paper.

PEORIA, ILLINOIS

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[9] C. E. Kendall, *Chemistry and Industry*, **63**, 211 (1944).

[10] M. Barker, L. Hunter and N. G. Reynolds, *J. Chem. Soc.* 874 (1948).