[Contribution from the Department of Chemistry of the Massachusetts Institute of Technology]

Aryl Carbamates of Cellulose Acetate

By W. M. Hearon and Jules L. Lobsitz

Phenyl and α-naphthyl isocyanates have been found to react readily with partially hydrolyzed cellulose acetates to produce colorless fibrous mixed esters with good solubilities in a variety of solvents.[1] The carbamate groups thus introduced are very resistant to acid hydrolysis and are only partially removed in alkaline media.[2] Recently, the reaction of chlorophenyl isocyanates with methyl cellulose has also been studied.[3]

We have now extended the study of the condensation of aryl isocyanates with partially hydrolyzed cellulose acetate to determine their relative rates of reaction, the solubilities of the products, and the ease of alkaline hydrolysis of the different carbamate groups. The relative rates of reaction of the isocyanates used at 2.5 times the theoretical with cellulose acetate containing 38.8% acetyl[3a] at 60° in order of increasing speed were as follows: *o*-tolyl, *p*-tolyl, phenyl, α-naphthyl, *o*-chlorophenyl and *p*-bromophenyl (see Fig. 1). The completely carbamated products were all soluble in acetone, pyridine, ethyl acetate, acetic acid, 1,4-dioxane, and chloroform, insoluble in methanol, and swollen in 75% ethyl aclohol. The phenyl, *p*-bromophenyl, and *o*-tolyl carbamates of cellulose acetate were soluble in cellosolve, while the *o*-chlorophenyl, *p*-tolyl, and α-naphthyl carbamates were merely swollen in the cold and soluble in that solvent hot.

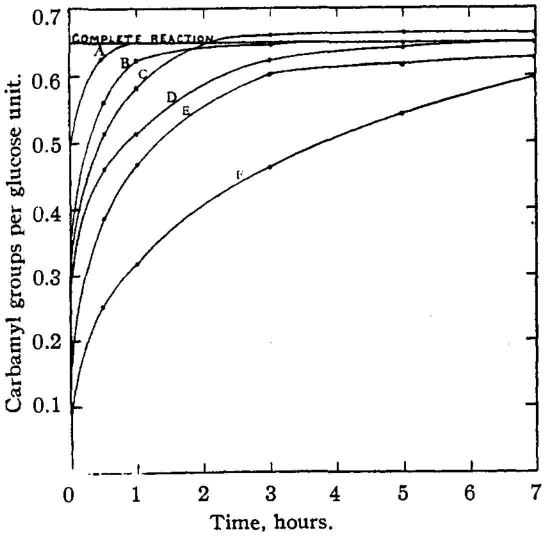

Fig. 1.—Rates of carbanilation of cellulose acetate (38.8% acetyl) with A, *p*-bromophenyl isocyanate; B, *o*-chlorophenyl isocyanate; C, α-naphthyl isocyanate; D, phenyl isocyanate; E, *p*-tolyl isocyanate; and F, *o*-tolyl isocyanate.

Determination of acetyl by the Eberstadt method[4] in cellulose acetate carbamates has been modified[2] to compensate for the carbamyl lost during the alkaline conditions. After the usual saponification, the excess alkali is back-titrated to an end-point, excess acid then added and the carbon dioxide removed by boiling. A second alkaline titration is then carried out to a second end-point. The carbamate hydrolyzed corresponds to the carbon dioxide lost while the acetyl accounts for the rest of the alkali consumed. Using this method on the acetate aryl carbamates formed, the acetyl values were determined and on the assumption, previously found true,[1] that no acetyl is lost during carbamation, the amount of carbamyl which entered has been calculated. The acetyl determinations have also indicated the amount of carbamyl hydrolyzed during the acetyl determination and these values are given in Table I. The values reported are, however, probably more a function of physical form of the ester than nature of the carbamate.

Table I

Hydrolysis of Carbamyl from Cellulose Acetate Carbamates after Forty-eight Hours of Saponification with 0.5 *N* Sodium Hydroxide

Cellulose acetate carbamates	% Carbamyl hydrolyzed	% Carbamyl originally	% of total carbamyl hydrolyzed
Phenyl	1.66	23.0	7.25
o-Chlorophenyl	9.45	27.8	34.0
p-Bromophenyl	1.98	33.2	5.97
o-Tolyl	2.37	25.1	9.46
p-Tolyl	1.24	25.1	4.96
α-Naphthyl	4.56	29.8	15.30

Experimental

Preparation of Carbamates.—The same procedure was followed for all rate studies. A 12.5-g. sample of cellulose acetate containing 38.8% acetyl, dried at 100° for forty-eight hours, was dissolved in 100 g. of dry pyridine and allowed to remain at 60° overnight in a tightly stoppered and previously dried flask. To the clear dope was added 2.5 times the theoretical of the isocyanate and the mixture was thoroughly shaken and left at 60 ± 0.5°. Samples were then withdrawn after 0.5, 1, 3, 5 and 7-hour intervals. Each sample was treated at once with 10 ml. of methanol to stop the reaction and precipitated into 600 ml. of rapidly stirred methanol. Purification of the white, fibrous product was completed by two additional precipitations into methanol from acetone dopes. The products were finally washed with water for two hours and dried at 60° for four hours. The yields in all cases were essentially quantitative. Acetyl analyses were carried out by the Eberstadt method[4] modified for carbamate[2] and gave the values listed in Table II.

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(1) Hearon, Hiatt and Fordyce, This Journal, **65**, 829 (1943).

(2) Hearon, Hiatt and Fordyce, *ibid.*, **65**, 833 (1943).

(3) Dyer and McCormick, *ibid.*, **68**, 986 (1946).

(3a) Kindly furnished by the Eastman Kodak Company, Rochester, New York.

(4) Genung and Mallatt, *Ind. Eng. Chem., Anal. Ed.*, **13**, 369 (1941).

TABLE II

ANALYSES OF CELLULOSE ACETATE CARBAMATES FROM CELLULOSE ACETATE OF 38.8% ACETYL

2.352 acetyls/glucose unit and 0.648 hydroxyls/glucose unit

Cellulose acetate carbamates	0.5 Hours		1 Hour		3 Hours		5 Hours		7 Hours		% Ac calcd. for complete reaction
	% Ac	Carb./ g. u.	% Ac	Carb./ g. u.	% Ac	Carb./ g. u.	% Ac	Carb./ g. u.	% Ac	Carb./ g. u.	
Phenyl	32.02	0.465	31.45	0.512	30.28	0.620	30.13	0.635	29.98	0.648	29.90
o-Chlorophenyl	29.15	.561	28.40	.624	28.20	.640	28.20	.640	28.05	.654	28.10
p-Bromophenyl	26.33	.627	26.10	.644	26.10	.644	26.10	.644	26.10	.644	26.00
o-Tolyl	34.48	.246	33.40	.317	31.40	.466	30.43	.536	29.80	.596	29.10
p-Tolyl	32.40	.388	31.35	.470	29.72	.600	29.56	.616	29.52	.619	29.10
α-Naphthyl	29.18	.512	28.17	.583	27.17	.665	27.17	.665	27.17	.665	27.30

Summary

1. Phenyl, *o*-chlorophenyl, *p*-bromophenyl, *o*-tolyl, *p*-tolyl, and α-naphthyl isocyanates reacted readily with 38.8% cellulose acetate at 60°.

2. The order of relative reaction rates of these isocyanates was as follows: *p*-bromophenyl (fastest), *o*-chlorophenyl, α-naphthyl, phenyl, *p*-tolyl, and *o*-tolyl (slowest).

3. The completely carbamated esters showed good solubilities in a variety of organic solvents.

4. All cellulose acetate carbamates formed hydrolyzed partially during deacetylation with aqueous alkali at room temperature.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Methyl Glucoside Carbanilates. II. α-Methyl-*d*-glucoside-2,3,6-tricarbanilate

BY W. M. HEARON

Carbanilates are excellent derivatives of methyl glucoside since they are readily formed, high melting, insoluble in water, readily crystallized and resistant to hydrolysis.

To the partially substituted methyl glucoside carbanilates previously reported[1] is now added the 2,3,6-tricarbanilate, which is of special interest because of its relation to carbanilated cellulose[2] and starch. The series of reactions for its preparation is given below

α-methyl-*d*-glucoside-2,3-dicarbanilate (I)

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6-trityl-α-methyl-*d*-glucoside-2,3-dicarbanilate (II)

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6-trityl-α-methyl-*d*-glucoside-2,3-dicarbaniliate-4-acetate (III)

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α-methyl-*d*-glucoside-2,3-dicarbanilate-4-acetate (IV)

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α-methyl-*d*-glucoside-2,3,6-tricarbanilate-4-acetate (V)

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α-methyl-*d*-glucoside-2,3,6-tricarbanilate (VI)

As with methyl-*d*-glucoside,[3] tritylation and acetylation of α-methyl-*d*-glucoside-2,3-dicarbanilate could be carried out without isolation of the intermediate. That no migration of acetyl to the primary hydroxyl[4] occurred during detritylation was proved by retritylation of IV to III. No migration of acetyl occurred during carbanilation since (V) melted sharply about 70° below α-methyl-*d*-glucoside-2,3,4-tricarbanilate-6-acetate which was prepared by acetylation of the 2,3,4-tricarbanilate.[1] Finally, no inversions or loss of methoxyl occurred during this series of reactions since carbanilation of VI gave the previously reported α-methyl-*d*-glucoside tetracarbanilate.[5]

Experimental

6-Trityl-α-methyl-*d*-glucoside-2,3-dicarbanilate (II).—A solution of 3.0 g. of α-methyl-*d*-glucoside-2,3-dicarbanilate[1] and 1.93 g. of trityl chloride in 6 ml. of dry pyridine was heated in a stoppered flask on a steam-bath for one hour. After cooling the solution was diluted with 20 ml. of ordinary pyridine and poured into cold water. The white precipitate, amounting to 4.8 g. or 98%, was recrystallized from hot methanol giving 3.1 g. or 63% yield melting at 121–122°; $[\alpha]^{25}\text{D}$ +57.3° (acetone, *C* 0.1).

Anal. Calcd. for $C_{40}H_{38}O_8N_2$: C, 71.2; H, 5.63; N, 4.16; trityl, 36.1. Found: C, 71.1; H, 5.75; N, 4.15; trityl, 36.2.

6-Trityl-α-methyl-*d*-glucoside-2,3-dicarbanilate-4-acetate (III). A. By Acetylation of 6-Trityl-α-methyl-*d*-glucoside-2,3-dicarbanilate.—A solution of 2.0 g. of 6-trityl-α-methyl-*d*-glucoside-2,3-dicarbanilate and 4.5 ml. of acetic anhydride in 10 ml. of dry pyridine was heated in a stoppered flask on a steam-bath for thirty minutes. After cooling to room temperature water was added to a permanent cloudiness and the mixture was poured into cold water. The precipitate, amounting to 2.1 g. or 99%, crystallized from hot alcohol giving 1.9 g. or a 90% yield, m. p. 134–135°, $[\alpha]^{25}\text{D}$ +77.8° (acetone, *C* 0.1).

Anal. Calcd. for $C_{42}H_{40}O_9N_2$: C, 70.4; H, 5.58; N, 3.91; trityl, 33.9. Found: C, 70.0; H, 5.80; N, 3.75; trityl, 33.8.

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(1) Hearon, Hiatt, and Fordyce, THIS JOURNAL, **66**, 995 (1944).

(2) Hearon, Hiatt and Fordyce, *ibid.*, **65**, 829 (1943).

(3) Helferich, Klein and Snyder, *Ber.*, **59**, 81 (1926).

(4) Compare Helferich and Bredereck, *ibid.*, **64**, 2413 (1931); Helferich and Müller, *ibid.*, **63**, 2146 (1930); Robertson, *J. Chem. Soc.*, **1933**, 737.

(5) Wolfrom and Pletcher, THIS JOURNAL, **62**, 1151 (1940).