solid was taken up in glacial acetic acid, and the solution poured over flaked ice. There was recovered 0.5 g. (91% yield) of yellow material, m.p. (out of alcohol–water) 320°.

Anal. Calcd. for $C_{26}H_{23}NO_4$: C, 75.58; H, 5.61; N, 3.39. Found: C, 75.62; H, 5.82; N, 3.62.

Attempted Preparation of Phthalone of Lower Melting Form II.—An intimate mixture of 2.3 g. of the isomeric substituted cinchoninic (lower melting form) produced in the preceding synthesis and 1.2 g. of phthalic anhydride was heated in an oil-bath for 3 hours. On working up as above there was recovered 1.72 g. of unreacted starting material (75% recovery). There was undoubtedly some decarboxylation of the acid to the corresponding substituted quinoline during the reaction period.

Preparation of 3-Alkyl-2-(2-cyclohexylethyl)-cinchoninic Acids.—The general procedure for the preparation of all substituted cinchoninic acids formed in this investigation was essentially the same. Only one compound was isolated in each of the other condensations even though a search was made for isomeric products. Thus, the condensation of 1-cyclohexyl-3-pentanone with isatin will be presented in detail as a sample preparation of the substituted cinchoninic acids formed which are summarized in Table III.

A mixture of 10.3 g. (0.06 mole) of 1-cyclohexyl-3-pentanone and 12.5 g. (0.08 mole) of isatin was dissolved in 36 ml. of 85% alcohol–water containing 31% by weight (0.12 mole) of potassium hydroxide. The solution then was heated on a steam-cone for 12 hours, cooled, diluted with 200 ml. of water and extracted with ether to remove unreacted ketone. After careful acidification with 50% acetic acid to *p*H 7.5 there was an immediate precipitation of gray micro-crystals. After sitting overnight in the refrigerator the solid was recovered and recrystallized from alcohol–water. There was obtained 9.0 g. (47% yield) of the substituted cinchoninic acid.

Frequently it was found desirable to remove excess water by centrifugation before filtering after the acidification step.

Attempted Condensation of 1-Cyclohexyl-4-methyl-3-pentanone with Isatin.—This particular condensation is unique, among those studied, in that in the ketone here utilized there is only one methylene group *alpha* to the carbonyl of the ketone. Therefore, only one cinchoninic acid is possible from the normal Pfitzinger condensation.

No substituted cinchoninic acid was obtained from any of the several experiments tried; usually the ketone was recovered in about 40% accountability as compared to a 60% accountability under comparable conditions using no isatin in the reaction mixture. In this connection, it is of definite interest to note that Mead and co-workers[15] attempted the condensation of isopropyl methyl ketone and isatin under the usual Pfitzinger conditions, but the anticipated 2-(1-methylethyl)-cinchoninic acid was not obtained.

(15) J. F. Mead, A. E. Senear and J. B. Koepfli, THIS JOURNAL, **68**, 2709 (1946).

AUSTIN, TEXAS

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE FORMER PHOSPHATE DIVISION, MONSANTO CHEMICAL CO.]

Carbamoylphosphonates[1]

BY THEODOR REETZ,[2] D. H. CHADWICK,[2] E. E. HARDY AND S. KAUFMAN[2]

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The carbamoylphosphonates, $RR'NCOPO(OR'')_2$, may be prepared through the Arbusov reaction, the Michaelis reaction, amidation of methyl dialkoxyphosphinylformate or reaction of dialkyl phosphite with an isocyanate. Of these preparative methods, that of Arbusov is the most practical and generally applicable.

The preparation and properties of the carbamoylphosphonates as a new[3] class of compounds was of interest because of the possibility of preparing them by the direct reaction of a dialkyl phosphite and an isocyanate. It is known that dialkyl phosphites will add to the carbonyl group[4] and to carbon–nitrogen double bonds,[5] and sodium bisulfite has been reported to add to isocyanates producing carbamoylsulfonates.[6] It therefore seemed probable that dialkyl phosphites would react with isocyanates to produce carbamoylphosphonates.

$$RNCO + HPO(OR')_2 \longrightarrow RNHCOPO(OR')_2$$

The only report[3] of a compound of this class is that of the parent diethyl carbamoylphosphonate, $H_2NCOPO(OC_2H_5)_2$, prepared by allowing a solution of ethyl diethoxyphosphinylformate and anhydrous ammonia in alcohol to stand for several weeks.[7]

Initial attempts to effect reaction between dialkyl phosphites and isocyanates, made at relatively low temperature to avoid possible reversion of the expected products to the starting materials, were not successful. Therefore, before pursuing this approach further, we turned to more general methods for the preparation of phosphonates.

The Arbusov reaction was found to be generally applicable for the preparation of diethyl alkyl- and dialkylcarbamoylphosphonates from the corresponding alkyl- and dialkylcarbamoyl chlorides

$$RR'NCOCl + (C_2H_5O)_3P \longrightarrow RR'NCOPO(OC_2H_5)_2 + C_2H_5Cl$$

R = alkyl, R′ = alkyl or hydrogen

The monoalkylcarbamoyl chlorides were prepared by passing the theoretical amount of anhydrous hydrogen chloride into the isocyanates, and they were used without further treatment.

The Michaelis reaction also was found to be applicable, as applied to the preparation of diethyl dimethylcarbamoylphosphonate

$$(CH_3)_2NCOCl + NaPO(OC_2H_5)_2 \longrightarrow (CH_3)_2NCOPO(OC_2H_5)_2$$

(1) Presented before the Division of Organic Chemistry at the 124th National Meeting of the American Chemical Society, Chicago, Ill., September, 1953.

(2) Organic Chemicals Div., Monsanto Chemical Co., St. Louis 4, Mo.

(3) Since this work was completed, it has come to our attention that B. A. Arbusov and N. I. Rizpolozhensky have reported the preparation of dialkyl diethylcarbamoylphosphonates: *Izvest. Akad. Nauk S.S.S.R., Otdel Khim. Nauk*, 847 (1952); *C. A.*, **47**, 10457 (1953). Their work and ours are complementary in that they varied the alkyl groups of the phosphonate esters, whereas we studied the preparation of a series of diethyl mono- and dialkylcarbamoylphosphonates by several synthetic routes.

(4) E. K. Fields, U. S. Patent 2,579,810 (1951); A. L. Morrison and F. R. Atherton, British Patent 682,706 (1952); A. N. Pudovik, *Zhur. Obshchei Khim. (J. Gen. Chem.)*, **22**, 462, 467, 473 (1952); V. S. Abramov, *ibid.*, **22**, 647 (1952); A. R. Stiles, U. S. Patent 2,593,213 (1952).

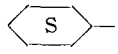
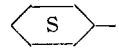
(5) E. K. Fields, THIS JOURNAL, **74**, 1528 (1952); A. N. Pudovik, *Doklady Akad. Nauk S.S.S.R.*, **83**, 865 (1952).

(6) S. Petersen, *Ann.*, **562**, 205 (1949).

(7) P. Nylen, *Ber.*, **57**, 1023 (1924).

TABLE I

CARBAMOYLPHOSPHONATES

RR'NCOPO(OC$_2$H$_5$)$_2$ R	R'	Prep. method[a]	Reacn. time hr.	Reacn. temp. max. °C.	Yield %	B.p., or m.p.[d] °C. 1 mm.	Phosphorus, % Calcd.	Phosphorus, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
H	H	C	6	40	69	M. 133–134				
CH_3	H	D	26	140	25	107(0.5 mm.)	15.87	14.78		
C_2H_5	H	A	1.5	70	41	104–105	14.81	14.40	6.70	7.49
		C	16	50	48	103–105	14.81	14.47	6.70	6.27
		D	8.5	136	47	104–107				
n-C_3H_7	H	C	16	35	80	109–110	13.88	14.17		
$(CH_3)_2CH$	H	C	72	45	61	100–102	13.88	14.21	6.27	6.34
C_6H_5	H	A	3	140	10	154–156[c]	12.04	12.93	5.45	4.95
		D	28	40	9	144–160[c]				
$(C_2H_5O)_2OPCONH(CH_2)CH_2$	H	C	1	60	66	M. 86–87	15.95	16.17	7.22	7.01
CH_3	CH_3	A	3	165	92	91–92	14.81	15.17		
		B	2.5	95	56(37)[b]	88–90				
		C	2.5	75	40	88	14.81	15.03	6.70	6.34
C_2H_5	C_2H_5	A	2.5	165	41	95–96	13.06	12.86	5.91	5.90
		C	16	55	Trace	92–94				
n-C_4H_9	*n*-C_4H_9	A	3	160	66	116	10.56	10.1		
$(CH_3)_2CHCH_2CH_2$	$(CH_3)_2CHCH_2CH_2$	A	3	160	31	129–131	9.64	9.21		
		A	3	160	100(crude)	dec.	8.97	3.42		

[a] A = Arbusov, B = Michaelis, C = Amidation, and D = from isocyanate. [b] 56% adding $NaPO(OC_2H_5)_2$ to $(CH_3)_2NCOCl$, 37% by reverse addition. [c] With some decomposition. [d] Uncorrected.

In accordance with the report[8] that a second mole of sodiophosphonate can add to the carbonyl group of the primary product to decrease the yield in the case of acetylphosphonates, it was found that addition of the sodiophosphonate to dimethylcarbamoyl chloride resulted in a significantly higher yield (56%) than the usual addition of the chloride to the sodiophosphonate (37%). Since the Arbusov reaction is a more convenient preparation and led to a considerably higher yield, the Michaelis method was not investigated further.

The original method of Nylen,[7] amidation of ethyl diethoxyphosphinylformate, also was investigated, and found to be generally applicable to the preparation of the monoalkyl compounds. Whereas Nylen allowed an alcoholic solution of ethyl diethoxyphosphinylformate and anhydrous ammonia to stand for two weeks, it was found that simply passing slightly less than the calculated quantity of ammonia into methyl diethoxyphosphinylformate at 40° resulted in rapid precipitation of the amide in good yields. Similarly, by adding primary amines to the phosphinylformate, the alkylcarbamoylphosphonates were obtained. The use of higher temperatures or excess amine led to markedly reduced yields. The reduced yields undoubtedly are due to further reaction of the amine with the carbamoylphosphonate, as discussed below. The amidation method was not generally applicable to the preparation of dialkylcarbamoylphosphonates; only a trace of diethyl diethylcarbamoylphosphonate was isolated, although a 40% yield of the dimethylcarbamoylphosphonate was realized. It is interesting to note that the yield of carbamoylphosphonates decreased in the order of increasing ionization constants of the amines in the case of the primary amines and also in the case of the secondary amines.

(8) A. E. Arbusov and M. M. Azanovskaya, *Doklady Akad. Nauk, S.S.S.R.*, **58**, 1961 (1947).

Finally, it was found possible, by employing higher temperatures and more drastic conditions than initially believed suitable due to expected decomposition of the products, to prepare the monoalkylcarbamoylphosphonates by reaction of isocyanates and dialkyl phosphites. This interesting reaction is apparently generally applicable, although yields were not high.

The carbamoylphosphonates prepared and the methods employed are summarized in Table I.

Infrared analysis confirmed the structures of the carbamoylphosphonates. In addition to bands in the region of 8.0, 9.7 and 6.0–6.2 μ, typical of the PO, P–O–C and C=O groups, respectively, (1) the parent diethyl carbamoylphosphonate showed a double band in the 3.0 μ region, typical of the N–H stretching vibration and (2) diethyl ethylcarbamoylphosphonate showed a band in the 3.0 μ region, typical of the N–H stretching vibration, and a band in the 6.4–6.6 μ range, typical of the C–N stretching vibration.

The carbamoylphosphonates were more stable thermally than might be expected. With the exception of diethyl phenylcarbamoylphosphonate and diethyl dicyclohexylcarbamoylphosphonate, all the compounds were sufficiently stable that they could be distilled *in vacuo* without difficulty. Some decomposition was evident during the distillation and redistillation of the phenylcarbamoylphosphonate, and the material collected in the Dry Ice trap protecting the oil-pump exhibited the odor of phenyl isocyanate. The dicyclohexylcarbamoylphosphonate could not be distilled.

The lower molecular weight carbamoylphosphonates are soluble in water, alcohol, acetone and similar solvents, but insoluble in hexane. The higher homologs, such as the N,N-dibutyl derivative, are insoluble in water. Compared to the acylphosphonates, the carbamoylphosphonates are more stable to hydrolysis than would be predicted.

The expected cleavage by amines of the carbamoylphosphonates to ureas and dialkyl phosphites was not observed. Rather, evidence was obtained for the somewhat surprising alkylation of the amines by the phosphonate ester. Thus, treatment of diethyl dimethylcarbamoylphosphonate with dimethylamine gave a product for which no distillate was obtained on attempted distillation *in vacuo*, although both tetramethylurea and diethyl phosphite boil below 200° at atmospheric pressure. Treatment of the carbamoylphosphonate with N-methylaniline permitted recovery of N-ethyl-N-methylaniline in about 63% yield.

Acknowledgment.—We wish to express our appreciation to Mr. D. R. Beasecker for determination and interpretation of the infrared spectra reported.

Experimental

Methyl Diethoxyphosphinylformate.[9]—Methyl chloroformate (294 g., 3.1 moles) was added to 560 g. (3.4 moles) of triethyl phosphite at 120° at such a rate as to maintain a steady evolution of ethyl chloride. Distillation of the crude product gave 483 g. (82%) of distillate boiling at 57–59.5° (1 mm.), which upon redistillation boiled at 58–59° (1 mm.).

Diethyl Carbamoylphosphonate.—When 1.4 g. (0.082 mole) of anhydrous ammonia was passed into 19.6 g. (0.1 mole) of methyl diethoxyphosphinylformate over a period of three hours at 40°, crystals began to precipitate shortly after ammonia addition was begun and continued to the end of the addition. The mixture was allowed to stand several hours, the crystals removed by filtration and twice recrystallized from benzene. After recrystallization the product weighed 12.5 g. (69% yield basis formate, 84% yield basis ammonia) and melted at 133–134°. Nylen[7] reports a melting point of 134°.

Diethyl Ethylcarbamoylphosphonate. (a) **Arbusov.**—Ethylcarbamoyl chloride was prepared by passing the calculated amount of anhydrous hydrogen chloride into ethyl isocyanate at 30°. Undistilled ethylcarbamoyl chloride (53.5 g., 0.5 mole) was added slowly to 90 g. (0.54 mole) of triethyl phosphite, the temperature of the mixture being maintained at 60°. After the addition was complete, the reaction mixture was maintained at 70° for 90 minutes, at which time 29.5 g., equivalent to 91% reaction, of ethyl chloride had collected in a cold trap. Upon distillation *in vacuo* a fraction weighing 42.5 g. (41%) was collected, which boiled in the expected temperature range. Upon redistillation the material boiled at 104–105° (1 mm.).

(b) **Amidation.**—Ethylamine (4.5 g., 0.1 mole) was passed into 19.6 g. (0.1 mole) of methyl diethoxyphosphinylformate, the temperature rising to and being maintained at 50° by cooling. After standing overnight at room temperature, the alcohol formed was removed under diminished pressure and the residual material distilled *in vacuo*. The fraction (10 g., 48%) boiling in the expected temperature range was redistilled twice to obtain 6.2 g. of product boiling at 103–105° (1 mm.).

(c) **From Isocyanate.**—A solution of 71.0 g. (1.0 mole) of ethyl isocyanate and 192 g. (1.4 moles) of diethyl phosphite was heated under reflux for 8.5 hours, during which time the temperature rose from 80 to 136°. Distillation under reduced pressure permitted recovery of 98.1 g. (47%) of diethyl ethylcarbamoylphosphonate boiling at 104–107° (1 mm.).

Diethyl Phenylcarbamoylphosphonate. (a) **Arbusov.**—Phenylcarbamoyl chloride (155 g., 1.0 mole) prepared by addition of an equimolar amount of anhydrous hydrogen chloride to phenyl isocyanate was added to 250 g. (1.5 moles) of triethyl phosphite at 125–130° over a period of one hour. The reaction mixture then was maintained at 140° for two hours. The ethyl chloride collected in a cold trap through which the reaction flask was vented totaled 55 g., equivalent to 85% reaction. Distillation gave a fraction of 144 g. boiling at 140–154° (1 mm.). Redistillation of 42 g. of this distillate fraction gave, in addition to lower boiling materials, only 7.7 g. of distillate boiling at 145–156° (1 mm.), of which 4.5 g. boiled at 154–156° (1 mm.). Decomposition was evident during the distillation of this fraction. The material (3.5 g.) that collected in the cold trap had the odor of phenyl isocyanate.

(b) **From Isocyanate.**—A solution of 11.9 g. (0.1 mole) of phenyl isocyanate and 13.8 g. (0.1 mole) of diethyl phosphite was maintained at 40° for 28 hours. Distillation under reduced pressure permitted recovery of 2.5 g. (9%) of product distilling, with some decomposition, at 144–160° (1 mm.).

Tetraethyl [Ethylenebis-(iminocarbonyl)]-diphosphonate. Amidation.—Ethylenediamine (6.0 g., 0.1 mole) was added dropwise to 47.8 g. (0.24 mole) of methyl diethoxyphosphinylformate at 60° with agitation. A vigorous reaction was observed. After a few minutes the methanol formed was removed under diminished pressure and the residual oil allowed to stand in the cold to crystallize. After recrystallizing twice from ether–carbon tetrachloride solution, the product (25.5 g., 66%) melted at 86–87°.

Diethyl Dimethylcarbamoylphosphonate. (a) **Arbusov.**—A solution of 107.5 g. (1.0 mole) of dimethylcarbamoyl chloride and 166 g. (1.0 mole) of triethyl phosphite was heated to 90°, whereupon an exothermic reaction was initiated, the temperature rising to and being maintained at 120° for 1.5 hours. The reaction mixture was then heated to 165° for about one hour. At the end of this time a total of 63 g. (equivalent to 98% reaction) of ethyl chloride had been collected in a cold trap through which the reaction flask was vented. Distillation of the reaction mixture permitted isolation of 192.5 g. (92%) of product boiling at 91–92° (1 mm.). Redistillation yielded a product which boiled at 88° (1 mm.).

(b) **Michaelis.**—A solution of sodium diethyl phosphite was prepared from 11.5 g. (0.5 mole) of sodium and 72.0 g. (0.52 mole) of diethyl phosphite in 250 ml. of xylene. This solution was added to a solution of 51 g. (0.48 mole) of dimethylcarbamoyl chloride in 100 ml. of xylene over a period of one hour, with cooling to 25°. The reaction mixture was then maintained at 95° for 1.5 hours, filtered to remove sodium chloride, and distilled. The phosphonate (58.5 g., 55.8%) boiled at 88–90° (1 mm.).

When the reaction was carried out in a similar fashion except that the carbamoyl chloride was added to the sodium diethyl phosphite, the yield was reduced to 38.3 g. (36.5%).

(c) **Amidation.**—Dimethylamine (12.7 g., 0.28 mole) was passed into 58.8 g. (0.29 mole) of methyl diethoxyphosphinylformate over a period of two hours, the temperature rising to and being maintained at 45 to 50°. The mixture was heated to 75° for about 20 minutes and then distilled *in vacuo*. A fraction of 23.5 g. (40%) was collected and twice redistilled, boiling at 88° (1 mm.).

Stability of Diethyl Dimethylcarbamoylphosphonate to Hydrolysis.—A solution of 20.9 g. (0.1 mole) of the phosphonate and 1.8 g. (0.1 mole) of water was allowed to stand at 30–35° for three days. Distillation permitted recovery of 19.5 g. (93%) of unchanged phosphonate, boiling at 88–89° (1 mm.).

When a like solution of phosphonate and water was heated under reflux for four hours, the temperature rose gradually from 128 to 131°. Distillation permitted recovery of 9.2 g. (44%) of unchanged phosphonate and a distillation residue of 7.1 g.

Reaction of Diethyl Dimethylcarbamoylphosphonate and Dimethylamine.—Dimethylamine was passed through 20.9 g. (0.1 mole) of the carbamoylphosphonate for three hours at increasing temperatures up to 100°. A viscous oil (23 g.) which could not be distilled under vacuum was obtained, rather than tetramethylurea (b.p. 177° at 760 mm.) and diethylphosphite (b.p. 187° at 760 mm.) as expected.

Reaction of Diethyl Dimethylcarbamoylphosphonate and N-Methylaniline.—The phosphonate (20.9 g., 0.1 mole) and N-methylaniline (10.9 g., 0.1 mole) were heated at 170° for 45 minutes, the product cooled and treated with a solution of 12 g. of sodium hydroxide and 50 ml. of water. The organic layer was separated, dried and distilled. The product (9.5 g.) boiled at 199.5–200°. N-Ethyl-N-methylaniline boils at 202°. Determination of the N-methylaniline content of the N-ethyl-N-methylaniline by the method of Berl-Lunge[10] indicated it to be about 10%. Thus the yield of N-ethyl-N-methylaniline was 63%.

(9) A. E. Arbusov and A. A. Dunin, *J. Russ. Phys. Chem. Soc.*, **46**, 295 (1914).

(10) Berl-Lunge, "Chemisch-technische Untersuchungsmethoden," Eighth Edition, Vol. 5, Julius Springer, Berlin, 1934, p. 1233.

Determination of Infrared Spectra.—The infrared spectra were measured over the wave length range of 2 to 16 microns using a Baird Spectrophotometer. The spectra of liquid samples were measured in capillary cells, those of solids as mineral oil mulls.

ST. LOUIS, MISSOURI

[CONTRIBUTION FROM THE NORTHERN UTILIZATION RESEARCH BRANCH[1]]

Preparation of Methyl Glycosides of Homologous α-1,6′-Linked Gluco-oligosaccharides and the Optical Rotation of their Cuprammonium Complexes[2,3]

BY T. A. SCOTT, JR., AND F. R. SENTI

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Cuprammonium complexes of several native dextrans were found to be much more levorotatory than was expected from the optical rotation of methyl glucopyranoside in cuprammonium solution and the structure of these dextrans indicated by periodate oxidation analysis. To determine the optical activity of cuprammonium complexes of α-1,6′-linked anhydroglucopyranoside units, free from effects of branching, the lowest members of the methyl isomaltoside homologous series were prepared by methanolysis of NRRL B-512 dextran. Eleven members, DP 1 through 11, were chromatographically separated on a cellulose column and were characterized by paper chromatograms, periodate oxidation analysis, tests for furanoside structure, reducing power, methoxyl content, and optical rotation at 4358 Å. in aqueous and cuprammonium solutions. For glycosides of *DP* greater than unity, the difference between the molecular rotation per anhydroglucose unit in cuprammonium and aqueous solutions was proportional to $(DP - 1)/DP$. From this relationship a value of −99,000° was determined for the molecular rotational shift of an α-1,6′-linked unit in a dextran molecule. It was concluded that the presence of a glucosyl unit on number 6 hydroxyl leads to a marked preference for complex formation at the 2,3-position compared with the 3,4-position.

The change in optical rotation caused by cuprammonium–glycol complexing has been used by Reeves[4] to assign ring conformations to methyl glycopyranosides and to determine qualitatively the predominant type of glycosidic linkage in polysaccharides. Reeves has shown that cuprammonium complexing at the 2,3-hydroxyl positions of methyl 4-methyl-D-glucopyranoside causes a decrease of 200,000° in the molecular rotation, whereas complexing at the 3,4-hydroxyl positions of methyl 2-methyl-D-glucopyranoside produces an increase of 210,000° in the molecular rotation. The molecular rotation of methyl D-glucopyranoside underwent an increase of only 25,000° in cuprammonium solution, presumably because of the compensating effects of complex formation at both the 2,3- and 3,4-positions. In each of the above cases the effect of cuprammonium–glucoside complexing on rotation was found largely to be independent of the anomeric configuration of the glucopyranoside.

Results on the glucopyranosides suggested that information on the glucosidic linkages in dextrans could be gained from the shift in optical rotation occurring on copper complex formation. Our measurements, however, on several native dextrans produced by different strains of *Leuconostoc mesenteroides* showed that dextrans in cuprammonium solution were much more strongly levorotatory than would be expected from the structures indicated by periodate oxidation analysis (see also 4). For example, NRRL B-512 dextran was found by periodate oxidation[5] to contain about 95% unbranched α-1,6′-linked D-anhydroglucopyranoside units, and this has been confirmed by methylation analysis.[6] Because of the availability of the 2-, 3- and 4-hydroxyls, these units would be expected to behave analogously to methyl D-glycopyranoside in the reaction with cuprammonium. The molecular rotation per anhydroglucose unit of this dextran, however, was found to decrease 90,000° in cuprammonium solution instead of increasing about 25,000°. Since the branched units in B-512 dextran have been shown[6] to carry linkages on position 3, these units could not form copper complexes, and, therefore, cannot be responsible for the anomalous rotational shift. It seemed, therefore, that the unbranched α-1,6-linked anhydroglucopyranoside units in dextran must themselves cause a rather large decrease in rotation in cuprammonium solution.

To gain further knowledge of the properties of the cuprammonium complexes of α-1,6′-linked anhydroglucopyranoside units, we prepared the lowest members of the methyl isomaltoside homologous series and determined their molecular rotations in aqueous and in cuprammonium solution. Glycoside derivatives of the oligosaccharides, required in order to confer the alkali stability needed for measurement of optical rotation in cuprammonium solution were obtained by methanolysis of a dextran to produce the methyl isomaltoside homologous series. The smallest members of the series were separated chromatographically on a large cellulose column. Although no one has reported the preparation of a homologous series of oligosaccharides by methanolysis of the parent polysaccharide, the analogous method of hydrolytic degradation is an established procedure. Whistler and Chen-Chuan Tu[7] have isolated the dimer through the

(1) One of the Branches of the Agricultural Research Service, U. S. Department of Agriculture. Article not copyrighted.

(2) From a thesis by Troy A. Scott, Jr., submitted to the Graduate School of Bradley University, Peoria, Ill., in partial fulfillment of the requirements for a M.S. degree.

(3) Presented before the Division of Carbohydrate Chemistry at the Meeting of the American Chemical Society in New York, N. Y., September 12–17, 1954.

(4) R. E. Reeves in "Advances in Carbohydrate Chemistry," Vol. 6, edited by W. W. Pigman and M. L. Wolfrom, Academic Press, Inc., New York, N. Y., 1951, p. 107.

(5) A. Jeanes and C. A. Wilham, THIS JOURNAL, **72**, 2655 (1950).

(6) J. W. Van Cleve, W. C. Schaefer and C. E. Rist, Abstracts of the 125th Meeting of the American Chemical Society, March, 1954, p. 8D.

(7) R. L. Whistler and Chen-Chuan Tu, THIS JOURNAL, **74**, 3609 (1952).