TABLE I

Substance	M. p., °C. (uncor.)	Rotation, $[\alpha]_D$ o	Temp., °C.	c	Solvent	Carbon Calcd.	Carbon Found		Hydrogen Calcd.	Hydrogen Found		Sulfur Calcd.	Sulfur Found	
Octamesylsucrose	86–94	+43.7	30.0	2.29	Acetone	24.8	24.7	24.7	3.93	3.89	3.95	26.5	26.4	26.2
Octatosylsucrose	82–86	+41.78	25.9	7.623	Chloroform	51.84	51.5	51.3	4.45	4.48	4.49	16.27	16.3	16.1
Tritosylsucrose[a]	66–69	+42.35	27.6	2.42	Chloroform	49.2	48.9	48.7	4.97	4.91	4.86	11.94	12.3	12.5
Pentaacetyltritosylsucrose[a]	58.5–61	+53.3	24.9	3.94	Chloroform	50.86	51.0	50.9	4.93	5.15	5.37	9.46	9.39	9.30

[a] Since the derivatives described here are not crystalline, their degree of homogeneity is not proved nor have their structures been determined by rigid methods. Nevertheless, because of the relatively great reactivity of primary hydroxyl groups in reactions of this type (*cf.* Hockett and Downing, THIS JOURNAL, **64**, 2463 (1942)) a strong presumption may be established to the effect that the *tri*substitution products described here consist almost entirely of the isomers to be expected from selective reaction at the three primary groups. The preparation of partially esterified sucrose derivatives gives rise to the need for a system of numbering the positions in the parent disaccharide. Helferich, Bohn and Winkler, *Ber.*, **63**, 994 (1930), have established a precedent for numbering the positions in a *reducing* disaccharide, cellobiose, by using plain numerals in the reducing moiety and numbers prime in the non-reducing section. In the case of sucrose, which is an unsymmetrical, non-reducing disaccharide, and in analogous cases we propose that plain numerals be used for numbering in the glucose moiety and numbers prime in the non-glucose part. Names for the two tosyl derivatives described above would be: 6,1′,6′-tri-(*p*-toluenesulfonyl)-sucrose and 2,3,4,3′,4′-pentaacetyl-6,1′,6′-tri-(*p*-toluenesulfonyl)-sucrose.

water. After drying over calcium chloride and removal of the chloroform *in vacuo*, a colorless amorphous product was collected. Pentaacetyltritosylsucrose was prepared by acetylating tritosylsucrose in pyridine according to conventional methods.

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Mechanism of the Formation of "Aldose Acetamides" in the Reaction of Acetylated Aldonic Acid Nitriles with Ammonia

BY R. C. HOCKETT, V. DEULOFEU AND J. O. DEFERRARI

When a fully acetylated aldonic acid nitrile is treated with aqueous ammonia, the main product is usually an open-chain "diacetamide derivative" of the aldose sugar having one less carbon atom[1]:

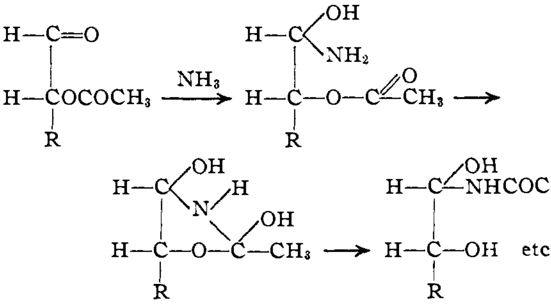
$$CH_2OAc(CHOAc)_4CN + NH_3 \longrightarrow CH_2OH(CHOH)_3CH(NHCOCH_3)_2 + NH_4CN + 3CH_3CONH_2$$

There is little doubt that the initial step of reaction is hydrolysis of the cyanide group as a pseudohalogen since in the presence of silver salts, silver cyanide is precipitated.[1b] The other product of such hydrolysis accompanied by deacetylation, would be expected to appear as the sugar with one less carbon atom in the chain.

The mechanism of the reaction whereby this newly formed aldose becomes combined with acetamide has been the subject of considerable experiment and speculation. Free aldoses do not show any tendency to combine directly with preformed acetamide, though this lack of affinity can be attributed reasonably to the hemiacetal structure of aldoses that have reached a state of equilibrium.

The assumption, moreover, that *aldehydo*aldose derivatives might combine directly with acetamide[2,1c] has not been sustained by later experimental findings. Pentaacetyl-*aldehydo*-D-glucose did not combine directly with acetamide under a variety of conditions, although this glucose derivative is converted by aqueous ammonia to the same glucose acetamide derivative which is the product of reaction of ammonia with the corresponding acetylated D-glucoheptonic acid nitrile.[1c,3]

It has therefore appeared that the observed sugar-acetamide derivatives must arise either as the products of interaction between acetamide and some unidentified sugar derivative that has only transitory existence during the course of the reactions, or through a mechanism that does not involve preformed acetamide at all. Isbell and Frush[4] have proposed a mechanism in line with modern theories of organic chemical reactions. They suggest that an acetylated *aldehydo* sugar may first add ammonia at the aldehyde group and that acetyl may then migrate to nitrogen from an ester group suitably located spacially in the same molecule to produce the acetamide-like structure



To test this hypothesis, we have caused tetraacetyl-L-arabonic acid nitrile to react with ethanolic ammonia in which 6.2 atom per cent. of the nitrogen is N^{15} while an excess of acetamide containing normal nitrogen was present in the alcohol solution. These results were obtained:

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(1) (a) Maquenne, *Compt. rend.*, **130**, 1402 (1900); (b) *cf.* Wohl, *Ber.*, **26**, 730 (1893); (c) Hockett and Chandler, THIS JOURNAL, **66**, 957 (1944).

(2) Brigl, Mühlschlegel and Schinle, *Ber.*, **64**, 2921 (1931); Deulofeu, *J. Chem. Soc.*, 2974 (1932).

(3) The product obtained in this case was actually "glucose monoacetamide" or N-acetyl-D-glucofuranosylamine, but the reaction mechanism involved in its formation is undoubtedly closely analogous to that which forms "aldose diacetamides" in other cases.

(4) Abstracts of papers for the 114th meeting of the American Chemical Society, Sept., 1948.

Experiment	1	2
Tetraacetyl-L-arabonic acid nitrile, moles	1	1
Normal acetamide in solution, moles	4	8
Excess of N^{15} in ammonia employed	6.2	6.2
Excess of N^{15} in L-erythrose diacetamide formed	5.69	5.71

In a control experiment, 100 mg. of acetamide was dissolved in ethanolic ammonia in which 6.2 atom per cent. excess of N^{15} was present. After forty-eight hours, evaporation of the ethanol yielded acetamide containing no N^{15}. From this it is evident that no detectable exchange of normal nitrogen and N^{15} took place under the conditions used.

These experiments suggest that "aldose diacetamides" do not arise from condensation of preformed acetamide with any sugar derivative, since if this occurred a larger proportion of N^{14} would be expected in the product, especially as the proportion of acetamide is increased in the environment (as in the second experiment). On the other hand an intramolecular mechanism such as that suggested by Isbell and Frush provides a simple explanation of the observations.

It will be noted that a small proportion of normal ammonia may be formed by hydrolysis of cyanide. The presence of a little normal ammonia could explain the slight dilution of N^{15}-rich ammonia that appears to have occurred, though this is scarcely greater than the experimental error.

Further experiments are in progress.

We wish to acknowledge our indebtedness to Dr. David Rittenberg and Miss Laura Ponticorvo of the Columbia University College of Physicians and Surgeons, Department of Biochemistry, for mass spectrometer determinations of N^{15}.

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Preparation of Radioactive Sulfur Dioxide from Barium Sulfate[1]

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There has been a need in this Laboratory for a simple and direct method for making radioactive sulfur dioxide from barium sulfate. At the present time the only method which has been used to convert radioactive barium sulfate to a chemically more useful form has been reduction at 900–1000° with carbon or hydrogen. This process has been carefully studied by Wells,[2] who has shown that good yields of barium sulfide (better than 90%) are obtained if the barium sulfate is heated rapidly to high temperatures. This precaution has not been observed by all workers.

One can then generate hydrogen sulfide from the barium sulfide, oxidize this to sulfur with triiodide solution,[3,4] and burn the sulfur after filtration of the resulting suspension. Apart from being tedious and indirect, this procedure is somewhat objectionable since sulfur dioxide prepared by combustion of sulfur is always contaminated by some sulfur trioxide which usually must be removed by an appropriate washing process. We find that combustion in oxygen of an intimate mixture of barium sulfate and red phosphorus gives a good yield of pure sulfur dioxide. Combustion in air gives poor yields.

The combustion was effected by means of a gas train consisting of the following: (1) drying tubes containing calcium chloride and "Caroxite" (a carbon dioxide absorbent), (2) a mercury blow-off valve, (3) a flow meter of the differential manometer type, (4) a combustion flask, (5) a tube containing glass wool to filter phosphorus pentoxide from the gas stream, (6) two glass spirals cooled with liquid oxygen, and (7) an aspirator. The combustion flask was made from a 1-liter filter flask by sealing on a short piece of tubing tangential to the bottom and was fitted at the top with a two-hole stopper carrying leads which terminated in a short length of resistance wire for ignition of the charge. The bottom of the flask was covered with a protective layer of clean sand prior to insertion, through the lower inlet, of an alundum boat containing the charge. The first of the two spirals (6), was of conventional design, but the second contained a plug of glass wool in a large (2 cm. o.d.) central tube to assure complete removal of sulfur dioxide from the gas stream. Most of the sulfur dioxide freezes as a loose powder which can easily undergo mechanical transfer beyond the refrigerated region; in practice the omission of the glass wool plug resulted in about 5% loss.

With a stream of oxygen passing through the lower tube of the combustion flask and out the upper side arm, the resistance wire was brought into contact with the charge and the charge ignited by passing a momentary current through the wire. Combustion is completed in less than thirty seconds. A one-liter container is sufficiently large that the flame will not come in contact with glass. The residue from the combustion is a metaphosphate glass containing unreacted barium sulfate.

It should be noted that if liquid air or liquid nitrogen instead of liquid oxygen were to be used as a refrigerant, it would be desirable that a manometer be attached to the gas train near the spirals, so that the oxygen pressure might be adjusted sufficiently low (15 cm. for liquid nitrogen, about 35 cm. for liquid air) to prevent condensation.

After sulfur dioxide had been collected in the

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[1] Published with the approval of the Oregon State College Monographs Committee, Research Paper No. 147, Department of Chemistry, School of Science.

[2] A. E. Wells, *J. Ind. Eng. Chem.*, **8**, 770 (1916).

[3] R. A. Cooley and D. M. Yost, THIS JOURNAL, **62**, 2474 (1940).

[4] G. L. Clark, S. G. Gallo and B. H. Lincoln, *J. Applied Phys.*, **14**, 428 (1943).