# **587.** *Ring Scission of Cyclic Acetals. Part I. The Formation of a Linear Polyester from* 1,3:2,4:5,6-*Tri*-O-*methylene*-D-*glucitol, Adipic Acid, and Trifluoroacetic Anhydride.*

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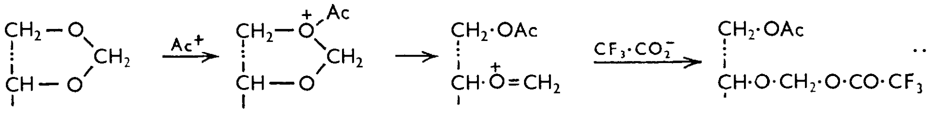
A new synthesis of linear polyesters from a cyclic acetal and a dicarboxylic acid is based on conversion of the latter by trifluoroacetic anhydride into a powerful acylating species having two active centres; the acetal must have two rings susceptible to scission by acylating reagents. Mild hydrolysis of the product, to remove trifluoroacetoxymethyl groups, leaves a polyester with free hydroxyl groups along the chain. The method has been employed with 1,3:2,4:5,6-tri-*O*-methylene-D-glucitol and adipic acid.

Trifluoroacetic anhydride converts simple carboxylic acids into powerful acylating agents,[1] which originate in the unsymmetrical anhydride known to be extensively formed in an equimolar mixture of the two reactants: [2]

$$\mathrm{R{\cdot}CO_2H + (CF_3{\cdot}CO)_2O \rightleftharpoons R{\cdot}CO{\cdot}O{\cdot}CO{\cdot}CF_3 + CF_3{\cdot}CO_2H} \quad . \; . \; . \; . \; . \quad (1)$$

Cyclic acetals of sugars [3] and hexitols [4] undergo ring scission with acylating agents, and in the acetolysis of hexitol diacetals and triacetals a notable feature is the marked difference in lability of the acetal rings; *e.g.*, the 2,4-*O*-methylenedioxy-ring is left intact [4] after acetolysis of 1,3:2,4:5,6-tri-*O*-methylene-D-glucitol, and the 2,5-*O*-methylenedioxy-ring in the reaction of 1,3:2,5:4,6-tri-*O*-methylene-D-mannitol; in both cases the other two rings open, to give *O*-acetyl groups at the primary carbon atoms and *O*-acetoxymethyl groups at the secondary carbon atoms. The same selectivity is shown towards tri-*O*-methyleneglucitol by an equimolar mixture of acetic acid and trifluoroacetic anhydride [5] in 4—5-fold molar excess over the acetal; with this reagent the attack on labile rings (*i.e.*, the 1,3- and 5,6-rings) is represented as in reactions (2). The bistrifluoroacetoxymethyl product is unstable and is not usually isolated; treatment with dry methanol readily converts it into 1,6-di-*O*-acetyl-2,4-*O*-methylene-D-glucitol. The ease of removal of the trifluoroacetoxymethyl groups by hydrolysis under conditions which do not affect the



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[1] Bourne, Stacey, Tatlow, and Tedder, *J.*, 1949, 2976.

[2] Bourne, Stacey, Tatlow, and Worrall, *J.*, 1954, 2006; Randles, Tatlow, and Tedder, *J.*, 1954, 436; Bourne, Stacey, Tatlow, and Worrall, *J.*, 1958, 3268.

[3] Schlubach, Ranchenberger, and Schultze, *Ber.*, 1933, **66**, 1248.

[4] Ness, Hann, and Hudson, *J. Amer. Chem. Soc.*, 1944, **66**, 665; *ibid.*, 1943, **65**, 2215; Barker and Bourne, *Adv. Carbohydrate Chem.*, 1952, **7**, 138.

[5] Bourne, Burdon, and Tatlow, *J.*, 1959, 1864.

acetyl groups is a unique feature that makes this method superior to degradation by acetolysis, since the product of the latter is not readily susceptible to selective hydrolysis.

The synthesis of a linear polyester from a cyclic acetal and a mixed anhydride of trifluoroacetic acid and a dibasic carboxylic acid depends on the presence of not more than two reactive acetal rings in the acetal. Since of the simple trialkylidenedioxy-derivatives of glucitol only the tri-*O*-methylene derivative contains a ring (2,4) completely resistant to acylating reagents, the investigation of polyester formation was begun with this derivative. The opening of the two labile rings (1,3- and 5,6-) with an adipic acid–trifluoroacetic anhydride reagent should produce a linear polymer, which after mild hydrolysis should contain two free hydroxyl groups per repeating unit of the chain. There is the possibility of an intramolecular reaction if the reactive acylating chain formed by the opening of one acetal ring attacked the other ring in the same acetal molecule; but since the cyclic derivative so formed would have to contain at least ten atoms, the occurrence of this reaction is unlikely in the general case and is highly improbable with tri-*O*-methyleneglucitol. A cyclic acetal with more than two labile rings would lead to branching in the polyester chain and the formation of a cross-linked product.

Free alcohol groups in the polyester are desirable because of the higher absorption of water which is possible through hydrogen-bonding and because of the possibility of high dye-uptake. At some inconvenience these groups can be obtained in polymer molecules by the use, before polymerisation, of blocking agents which are subsequently removed, but by the trifluoroacetic anhydride method the hydroxy-polyester is obtained directly.

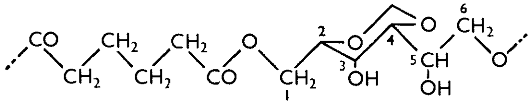
To test the method with 1,3:2,4:5,6-tri-*O*-methylene-D-glucitol and adipic acid equimolar quantities of the two reactants were dissolved in an excess of trifluoroacetic anhydride and left at room temperature for some hours. Volatile constituents were then removed under reduced pressure and the residue treated with aqueous sodium hydrogen carbonate. If the alkaline mixture was left for only a few hours before separating the insoluble product formed, it was found that the latter subsequently decomposed in the presence of atmospheric moisture liberating formaldehyde, thus showing that hydrolysis of the trifluoroacetoxymethyl groups was incomplete. Trifluoroacetic acid would also result from attack by atmospheric moisture, and might catalyse hydrolysis of the adipate ester groupings. This difficulty was overcome by continuing the alkali treatment for a few days, whereafter the insoluble polyester was stable to moisture. The polyester product was a colourless, brittle solid melting at 130—150° to a viscous liquid which could be drawn into brittle threads. The solid became swollen in some solvents and dissolved completely in pyridine. As expected, alkaline hydrolysis yielded adipic acid and crystalline 2,4-*O*-methylene-D-glucitol: the only other carbohydrate constituent detected by chromatography was a trace of glucitol.

A linear polymer made up of alternate 2,4-*O*-methylene-D-glucitol and adipic acid units linked through ester groups was therefore indicated.

The infrared absorption spectrum showed strong absorption by alcoholic hydroxyl groups at 3450 and 1075 cm.$^{-1}$ and by aliphatic carboxylate ester groups at 1726 cm.$^{-1}$ and in the region 1250 and 1180 cm.$^{-1}$ No absorption characteristic of fluorinated esters was detected. A weak band at 2770 cm.$^{-1}$ and a band at 1030 cm.$^{-1}$ indicated a cyclic ether. A medium band at 1565 cm.$^{-1}$ suggested the presence of the carboxylate ion which is also known to give rise to absorption at 1375 cm.$^{-1}$. When the polymer was boiled with N-hydrochloric acid for one minute and then dried at 90° the band at 1565 cm.$^{-1}$ disappeared. No change in intensity was evident in the 1375 cm.$^{-1}$ region but this may be due to the high level of absorption in this range. If it is assumed that the absorption coefficients of the carboxylate ester and carboxylate ion group are the same, the ratio of the optical densities of the two groups indicates that there are ten ester to one carboxylate ion group. This result does not permit calculation of the average chain length of the molecules, however, since individual chains may have two, one, or no carboxylic end groups.

Viscosities of solutions of the polymer in pyridine were measured at different concentrations and the intrinsic viscosity, $[\eta]$, was evaluated.[6] This is related to the average molecular weight, $M$, by the empirical expression $[\eta] = KM + K_0$, where the constants $K$ and $K_0$ are calculated from the viscosity of a similar type of polymer of known molecular weight in the same solvent and at the same temperature. No values are available for a polyester in pyridine; using data for polydecamethyleneglycol adipates in chlorobenzene [7] at 25° leads to a weight-average molecular weight of *ca.* 4900, corresponding to an average of 16 2,4-*O*-methylene-D-glucitol adipate residues per chain.

If the same mechanism operates with adipic as with acetic acid,[5] the ester groups in the polymer should be at positions 1 and 6 of the glucitol, giving the structure (I):



(I)

The polymer has a softening point of 88°. Its molecular weight appears to be too low to provide a useful basis for a synthetic fibre but the method of synthesis does not preclude the formation of products of higher molecular weight.

## EXPERIMENTAL

*Reaction of Adipic Acid–Trifluoroacetic Anhydride with* 1,3:2,4:5,6-*Tri*-O-*methylene*-D-*glucitol*.—Trifluoroacetic anhydride [1] (7·6 ml., 6·0 mol.) was added to the acetal (2·0 g.) and adipic acid (1·34 g., 1 mol.); the solids dissolved rapidly with evolution of heat to give a viscous coloured solution. After 3 hr. at room temperature, the volatile constituents were removed at 40° under reduced pressure. Anhydrous carbon tetrachloride was added and the solution evaporated to remove remaining traces of volatile matter; this process was repeated twice and gave a viscous transparent residue (6·46 g.). 10% Aqueous sodium hydrogen carbonate (75 ml.) was added and the mixture left at room temperature for 72 hr. The insoluble residue was filtered off, washed with water, and dried in a vacuum-desiccator. The resulting colourless brittle solid (2·13 g.) softened to a viscous liquid over the range 110—120°. A second specimen, obtained by the same method, melted over the range 130—150°. The melt could be drawn into threads which became brittle on cooling. The solid swelled and then dissolved completely in pyridine; it also swelled in chloroform and benzene but did not dissolve completely in either. It did not dissolve or swell in water. The products of alkaline hydrolysis were obtained by refluxing the solid (0·49 g.) with 0·1N-sodium hydroxide (30 ml.) for 30 min. The solution was cooled, acid was added to give pH 8, the mixture was evaporated to dryness, and the solid residue extracted with boiling pyridine (soluble component, A). The insoluble residue was dissolved in water, and acid was added to give pH 4. After evaporation to dryness, the residue was again extracted with pyridine to give a soluble component, B. The extract containing A was evaporated to give a brown solid, an ethanol extract of which was shown by chromatography to contain 2,4-*O*-methylene-D-glucitol and a trace of glucitol; the former (0·1 g., 33%) was obtained from the ethanol extract and had m. p. and mixed m. p. 161—162°, $[\alpha]_D^{18}$ $-11{\cdot}7°$ ($c$ 0·64 in $H_2O$). The extract containing B yielded a brown solid, soluble in water. The aqueous solution was brought to pH 9 and evaporated to dryness. Examination of the residue by paper chromatography showed the presence of adipic acid; the residue was converted into its *S*-benzylisothiouronium derivative (0·15 g., corresponding to a 52% yield of adipic acid from the polymer), m. p. and mixed m. p. 160°. Analysis of the polyester gave C, 47·6, and H, 6·7%.

Viscosity and density determinations were carried out on solutions of the polymer in pyridine which were first filtered and analysed by titration with standard alkali. Viscosities were measured at 25·4° with an Ostwald viscometer [6] which had been calibrated with water. The viscosities of the pyridine solutions are recorded in the Table as specific viscosities, $\eta_{sp}$, and relative viscosities, $\eta_r$, where $\eta_{sp} = (\eta - \eta_0)/\eta_0 = \eta_r - 1$; $\eta$ is the viscosity of the solution in

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[6] " Physical Methods of Organic Chemistry," Vol. I, ed. A. Weissberger. Interscience Publ. Inc., New York, 1945.

[7] Flory and Stickney, *J. Amer. Chem. Soc.*, 1940, **62**, 3032.

poises, and $\eta_0$ that of pure pyridine; $t$ is the time of flow in seconds, $c$ the concentration in g. of polymer per 100 ml. of pyridine solution, and $\rho$ the density of the solution in g./ml.

*Viscosities of polymer solutions in pyridine at* 25°.

| | $c$ | $t$ | $\rho$ | $10^2\eta$ | $\eta_{sp}$ | $\eta_r$ |
|---|---|---|---|---|---|---|
| Water ............... | — | 225·4 | 0·9969 | 8·824 | — | — |
| Pyridine ............ | — | 229·6 | 0·9782 | 8·818 | — | — |
| Soln. A ............ | 0·8405 | 262·3 | 0·9812 | 10·15 | 0·1510 | 1·1510 |
| ,, B ............ | 0·4946 | 248·4 | 0·9806 | 9·564 | 0·08457 | 1·0846 |
| ,, C ............ | 0·1602 | 235·1 | 0·9801 | 9·050 | 0·02630 | 1·0263 |

The intrinsic viscosity $[\eta]$ of the polymer was determined by plotting $\eta_{sp}/c$ against $c$ and measuring the intercept which the linear plot makes with the $\eta_{sp}/c$ axis. The value obtained was 0·165. Using the data for polydecamethyleneglycol adipates in chlorobenzene at 25° (see above) gives $K = 2{\cdot}12 \times 10^{-5}$, $K_0 = 0{\cdot}06$, from which, with $[\eta] = 0{\cdot}165$, the calculated value of $M$ is *ca.* 4900.

*Infrared Spectra.*—These were determined at the research laboratories of British Nylon Spinners Ltd., Pontypool, Mon., where $X$-ray examination, moisture uptake, and softening points were also recorded. The authors are indebted to Dr. W. A. W. Cummings for arranging this work and for interpretations of the spectral results which were obtained on a Perkin–Elmer spectrometer with a sodium chloride prism. The sample was heated to 100° between sodium chloride plates and these were pressed together to give a film.

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