224. *Polyamides Containing Carbohydrate Residues.*

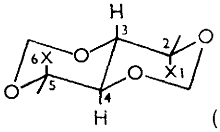
By T. P. Bird, W. A. P. Black, E. T. Dewar, and J. B. Hare.

Polyamides with high inherent viscosities have been prepared by interfacial polycondensation. Several new carbohydrate diamines and diacid chlorides are described.

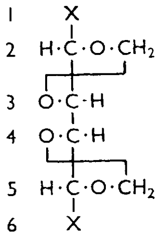
Previous attempts[1] to prepare polyamides of the Nylon-type from 1,6-diamino-1,6-dideoxy-2,4:3,5-di-*O*-methylene-D-mannitol and dibasic acids were unsuccessful owing to the high temperatures ($>200°$) necessary in the conventional melt-polymerisation used for the production of Nylon. All the polymers were dark and fibres drawn from the cooling melt were brittle and failed to exhibit the property of " cold drawing " which is characteristic of Nylon fibres. Polyamides of low molecular weight have been obtained[2] by reaction of tetra-*O*-acetylgalactaroyl dichloride with ethylenediamine and with piperazine, but these acetylated polymers were insoluble in common organic solvents and decomposed above 250° with no evidence of melting. Diamines have also been condensed at high temperatures with acetals and ketals of galactaric acid to give linear polyamides.[3]

The new technique of interfacial polycondensation[4] is well suited to carbohydrate monomers because of the low temperatures required for polymerisation, and we have used it to prepare carbohydrate polyamides with viscosities comparable to those of commercial Nylon. Two series of high-viscosity methylenedioxy-derivatives have been prepared: (1) from a 1,6-diamino-1,6-dideoxy-di-*O*-methylenehexitol and sebacoyl or adipoyl dichloride, and (2) from hexamethylenediamine or decamethylenediamine and a di-*O*-methylenehexaroyl dichloride. Other polyamides have also been prepared, including an isopropylidenedioxy-derivative by polycondensation of sebacoyl dichloride with 1,6-diamino-1,6-dideoxy-di-*O*-isopropylidenegalactitol.[5]

Di-*O*-methylenegalactaroyl dichloride[6] and 1,6-diamino-1,6-dideoxy-di-*O*-methylenegalactitol[7] were originally assigned the 2,4:3,5-di-*O*-methylene structure on the basis of the empirical rules deduced by Barker, Bourne, and Whiffen[8] for acetal rings in polyhydric alcohols. If this structure were correct, then both compounds would have a *trans*-bicyclic system (I; X = COCl or $CH_2 \cdot NH_2$) with both 1- and 6-residues X axial. It is probable,



(I)



(II)

although not proved, that the 2,3:4,5-diacetal with two α-*trans*-rings (II) is the more stable.[9] Similarly, the acetone residues in 1,6-diamino-1,6-dideoxy-di-*O*-isopropylidenegalactitol[5] probably also bridge the 2,3:4,5-positions.

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[1] Hamamura and Otsuka, *J. Agric. Chem. Soc. Japan*, 1942, **18**, 1092; Haworth, Heath, and Wiggins, *J.*, 1944, 155; Wiggins, *J.*, 1946, 384.

[2] Wolfrom, Toy, and Chaney, *J. Amer. Chem. Soc.*, 1958, **80**, 6328.

[3] Butler and Lawrance, B.P. 750,822/1956.

[4] Wittbecker and Morgan, *J. Polymer Sci.*, 1959, **40**, 289 and succeeding papers in that series.

[5] Bird, Black, Dewar, and Hare, *Chem. and Ind.*, 1961, 1077.

[6] Butler, Lawrance, and Stacey, *J.*, 1958, 740.

[7] Butler and Cummings, *J.*, 1956, 636.

[8] Barker, Bourne, and Whiffen, *J.*, 1952, 3865.

[9] Mills, *Adv. Carbohydrate Chem.*, 1955, **10**, 1.

1,6-Diamino-1,6-dideoxy-di-*O*-methylene-D-glucitol dihydrochloride, 1,6-diamino-1,6-dideoxy-di-*O*-methylene-L-iditol, di-*O*-methylene-D-glucaroyl dichloride, and di-*O*-methylene-L-idaroyl dichloride have been synthesised by us for the first time. These compounds have a 2,4:3,5-acetal structure.[9]

The polyamides were prepared by the " stirred interfacial polycondensation " technique of Beaman and his co-workers,[10] and some of their properties are given in Tables 1 and 2. In most cases high inherent viscosities were readily obtained with stringently purified monomers. We have confirmed the conclusion of Morgan and his associates[4] that the most important requirement for obtaining polymers of high molecular weight is the use of pure monomers. Other variables of interfacial polycondensation, such as type of organic solvent, use of emulsifying agent, type of acid acceptor, and rate of addition of acid chloride solution, had little effect upon viscosity. Temperature, however, was important,

TABLE 1.

Properties of polyamides.

Polyamide	Yield (%)	Found (%) C	Found (%) H	Found (%) N	Formula of unit	Required (%) C	Required (%) H	Required (%) N	η_{inh} in *m*-cresol	$[\alpha]_D$ (*c* 0·5; *m*-cresol)	Polymer-melt temp.
Poly-(1,6-dideoxy-di-*O*-methylene-1-sebacamidogalactitol) (A)	81·0	57·9	8·2	7·6	$C_{18}H_{30}N_2O_6$	58·4	8·2	7·6	1·00	0·0	203—205°
Poly-(1-adipamido-1,6-dideoxy-di-*O*-methylene-galactitol) (B)	49·9	52·8	7·0	8·3	$C_{14}H_{22}N_2O_6$	53·5	7·1	8·9	0·36	0·0	226—235
Poly-(1,6-dideoxy-di-*O*-methylene-1-sebacamido-D-glucitol) (C)	55·9	57·7	8·2	7·0	$C_{18}H_{30}N_2O_6$	58·4	8·2	7·6	1·20	−8 ± 2	>270 *
Poly-(1,6-dideoxy-di-*O*-methylene-1-sebacamido-L-iditol) (D)	80·8	57·3	8·2	7·3	$C_{18}H_{30}N_2O_6$	58·4	8·2	7·6	0·91	−69	>320 *
Poly-(1,6-dideoxy-di-*O*-methylene-1-sebacamido-D-mannitol) (E)	41·0	58·4	8·2	7·4	$C_{18}H_{30}N_2O_6$	58·4	8·2	7·6	1·02	+85	166—168
Poly-(hexamethylene di-*O*-methylenegalactaramide) (F)	77·4	53·3	7·2	8·75	$C_{14}H_{22}N_2O_6$	53·5	7·1	8·9	0·97	0·0	200—210
Poly-(hexamethylene di-*O*-methylene-D-glucaramide) (G)	68·2	51·6	7·2	8·4	$C_{14}H_{22}N_2O_6$	53·5	7·1	8·9	1·08	+56	>270 *
Poly-(hexamethylene di-*O*-methylene-L-idaramide) (H)	55·9	52·8	7·2	8·7	$C_{14}H_{22}N_2O_6$	53·5	7·1	8·9	0·95	+284	>320 *
Poly-(decamethylene di-*O*-methylene-L-idaramide) (I)	48·6	57·7	8·2	7·3	$C_{18}H_{30}N_2O_6$	58·4	8·2	7·6	0·73	+238	>320 *
Poly-(1,6-dideoxy-di-*O*-isopropylidene-1-sebacamidogalactitol) (J)	63·1	61·3	8·9	6·35	$C_{22}H_{38}N_2O_6$	61·9	9·0	6·6	0·94	0·0	125—135
Poly-(hexamethylene tetra-*O*-acetylgalactaramide) (K)	39·9	52·3	6·8	6·2	$C_{20}H_{30}N_2O_{10}$	52·4	6·6	6·1	0·34	0·0	>270 *
Poly-[1,6-dideoxy-di-*O*-methylene-1-(di-*O*-methylenegalactaramido)galactitol] (L)	24·1	47·4	5·7	6·6	$C_{16}H_{22}N_2O_{10}$	47·8	5·5	7·0	0·39	0·0	180—185
Poly-(1,6-dideoxy-di-*O*-methylene-1-terephthalamidogalactitol) (M)	91·9	56·5	5·6	8·0	$C_{16}H_{18}N_2O_6$	57·5	5·4	8·4	0·61	0·0	265—275
Poly-(1,6-dideoxy-di-*O*-methylene-1-terephthalamido-D-mannitol) (N)	78·7	55·9	5·7	8·1	$C_{16}H_{18}N_2O_6$	57·5	5·4	8·4	0·65	+83	220—230

* Decomp.

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[10] Beaman, Morgan, Koller, Wittbecker, and Magat, *J. Polymer Sci.*, 1959, **40**, 329.

and condensations were carried out at 0° to minimise hydrolysis of the acid chloride. A high viscosity was not obtained for the polymer (B) from diaminodimethylenegalactitol and adipoyl dichloride owing to the rapid hydrolysis of this acid chloride in the carbon tetrachloride–aqueous sodium hydroxide system. Low viscosities were also recorded for polymer (K) (from hexamethylenediamine and tetra-*O*-acetylgalactaroyl dichloride) and for the " all carbohydrate " polyamide (L) (from diaminodimethylenegalactitol and dimethylenegalactaroyl dichloride).

Elemental analyses in some cases differed slightly from theory and this is believed to be due to the difficulty of washing and drying these polymers, particularly when they were precipitated in a rubbery form. The same difficulty was not experienced with fibrous materials. Polyamides containing D-glucose, L-idose, or D-mannose residues were optically active. Polymers (C) and (D) have negative rotations, while the monomeric diaminodimethylenehexitols have positive rotations in *m*-cresol, so that polycondensation results in inversion. The idaric acid polyamides (H) and (I) show a high positive rotation compared with that of the acid chloride, but a comparable increase is not observed for the epimeric glucaric acid polyamide (G). Some of the polymers melted to clear, viscous liquids, while those containing di-*O*-methylene-D-glucose or di-*O*-methylene-L-idose residues decomposed without melting or softening. Polymer (K) was also infusible. There was a wide variation in solubility (Table 2).

TABLE 2.

Solubilities of polyamides in the solvent specified [soluble cold (++), soluble hot (+), insoluble (—)].

Polyamide	$CHCl_3$	$H{\cdot}CO{\cdot}NMe_2$	Me_2SO	$H{\cdot}CO_2H$	*m*-Cresol
(A)	—	—	+	++	++
(B)	—	++	++	++	++
(C)	—	—	—	—	++
(D)	—	—	—	+	+
(E)	—	++	++	++	++
(F)	—	+	+	++	++
(G)	++	++	++	++	++
(H)	—	—	—	++	++
(I)	—	—	—	++	++
(J)	++	++	++	++	++
(K)	—	++	++	++	++
(L)	++	++	++	++	++
(M)	—	—	+	+	+
(N)	—	++	++	++	++

EXPERIMENTAL

Materials.—Eastman Kodak Co.'s hexamethylene- and decamethylene-diamine were used without purification. Thionyl chloride was purified by Cottle's procedure.[11] Eastman Kodak Co.'s adipoyl dichloride was redistilled at <1 mm. Sebacoyl dichloride, prepared from sebacic acid and thionyl chloride [12] and distilled twice under reduced pressure, had b. p. 130°/0·9 mm., n_D^{18} 1·4685. Terephthaloyl dichloride (from Imperial Chemical Industries Limited) was recrystallised from dry hexane, then having m. p. 80—82°.

General Methods.—Specific rotations were measured at 20° in a 2-dm. tube. M. p.s were recorded on a Kofler hot-stage. Polymer-melt temperatures were measured either on a Kofler hot-stage or in a sealed tube under nitrogen. When viewed under the microscope in transmitted light, the interfacial polyamides appeared as dark, opaque, amorphous lumps, which became transparent and coalesced to a clear, viscous liquid over a temperature range which was taken as the polymer-melt temperature. Inherent viscosity $[\eta_{inh} = \ln(\eta_{soln.}/\eta_{solv.})/c]$ was determined in *m*-cresol at 25° at a concentration (c) of 0·5 g. polymer per 100 ml.; results are expressed in dl./g.

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[11] Cottle, *J. Amer. Chem. Soc.*, 1946, **68**, 1380.

[12] Filler, Fenner, Stokes, O'Brien, and Hauptschein, *J. Amer. Chem. Soc.*, 1953, **75**, 2693.

Products are described in Tables 1 and 2.

1,6-*Diamino*-1,6-*dideoxy*-2,3:4,5-*di*-O-*methylenegalactitol Dihydrochloride*.—The free diamine, prepared from galactitol as described by Butler and Cummings[7] and redistilled three times, had b. p. 106—108°/0·04 mm. This compound gave only a moderate viscosity (η_{inh} *ca.* 0·6) on condensation with sebacoyl dichloride, and was purified further by conversion into its dihydrochloride[7] which was recrystallised from aqueous ethanol. The dihydrochloride was used in condensations.

1,6-*Diamino*-1,6-*dideoxy*-2,4:3,5-*di*-O-*methylene*-D-*mannitol Dihydrochloride*.—The diamine was prepared as described by Haworth *et al.*,[1] giving $[\alpha]_D$ +93° (*c* 1·2 in *m*-cresol), and purified by conversion into its dihydrochloride,[1] $[\alpha]_D$ +65° (*c* 0·6 in H_2O) (Found: C, 33·8; H, 6·55; Cl, 24·9; N, 9·5. Calc. for $C_8H_{16}N_2O_4,2HCl$: C, 34·7; H, 6·5; Cl, 25·6; N, 10·1%).

1,6-*Diamino*-1,6-*dideoxy*-2,4:3,5-*di*-O-*methylene*-D-*glucitol Dihydrochloride*.—1,6-Dichloro-1,6-dideoxy-2,4:3,5-di-*O*-methylene-D-glucitol[13] (6·7 g.) was treated with 31% w/v aqueous ammonia solution (120 ml.) at 110—115° for 24 hr. in an autoclave. The solution was evaporated to dryness, the solid dissolved in water (75 ml.), and the solution passed through a column of Amberlite resin IRA-401 (OH^- form) to remove chloride. The eluate was concentrated, and the crude diamine (5·07 g.) was dissolved in water (10 ml.), concentrated hydrochloric acid (5·7 ml.) added at 0°, and crystallisation effected by addition of ethanol (20 ml.). The product was recrystallised three times from aqueous ethanol, to give 1,6-*diamino*-1,6-*dideoxy*-2,4:3,5-*di*-O-*methylene*-D-*glucitol dihydrochloride* (2·17 g., 28%), $[\alpha]_D$ +36·8° (*c* 1 in H_2O) (Found: C, 34·2; H, 6·45; Cl, 25·0; N, 9·9. $C_8H_{16}N_2O_4,2HCl$ requires C, 34·7; H, 6·5; Cl, 25·6; N, 10·1%). The free diamine had $[\alpha]_D$ +12° ± 1° (*c* 0·5 in *m*-cresol).

1,6-*Dichloro*-1,6-*dideoxy*-2,4:3,5-*di*-O-*methylene*-L-*iditol*.—2,4:3,5-Di-*O*-methylene-L-iditol[14] (2 g.) was suspended in dry pyridine (17 ml.), thionyl chloride (10 ml.) added, and the mixture refluxed at 100° for 30 min. The product was worked up as described[13] for the glucitol derivative, the yellow solid (1 g.) recrystallised from ethanol (200 ml.), and the crystals were extracted with carbon disulphide to remove contaminating sulphur, giving 1,6-*dichloro*-1,6-*dideoxy*-2,4:3,5-*di*-O-*methylene*-L-*iditol* (533 mg., 22·5%), m. p. 236·5—237°, $[\alpha]_D$ +64·4° (*c* 1·4 in $CHCl_3$) (Found: C, 39·1; H, 5·2; Cl, 29·3. $C_8H_{12}Cl_2O_4$ requires C, 39·5; H, 5·0; Cl, 29·2%).

1,6-*Diamino*-1,6-*dideoxy*-2,4:3,5-*di*-O-*methylene*-L-*iditol*.—Dichlorodimethyleneiditol (2·2 g.) was treated with 31% w/v aqueous ammonia (40 ml.) at 110—115° for 24 hr. as described above for the glucitol derivative, and the crude diamine (1·283 g.) sublimed at 180°/0·05—0·1 mm., to give the pure *product* (685 mg., 37%) as needles, m. p. 210—212° (decomp.), $[\alpha]_D$ +19° (*c* 0·5 in *m*-cresol) (Found: C, 47·2; H, 7·9; N, 13·5. $C_8H_{16}N_2O_4$ requires C, 47·1; H, 7·9; N, 13·7%).

1,6-*Diamino*-1,6-*dideoxy*-2,4:3,5-*di*-O-*methylene*-L-*iditol Dihydrochloride*.—Diaminodimethyleneiditol (1·213 g.) in water (2·5 ml.) was treated at 0° with concentrated hydrochloric acid (1·4 ml.) and ethanol (10 ml.), to give crystalline 1,6-*diamino*-1,6-*dideoxy*-2,4:3,5-*di*-O-*methylene*-L-*iditol dihydrochloride* (832 mg., 50%), $[\alpha]_D$ +13° (*c* 0·5 in H_2O) (Found: C, 34·3; H, 6·6; Cl, 25·2; N, 9·8%).

1,6-*Diamino*-1,6-*dideoxy*-2,3:4,5-*di*-O-*isopropylidenegalactitol*.—This diamine was prepared as described in a preliminary note[5] and redistilled twice; it had b. p. 96—98°/0·05 mm., m. p. 75·5—76°.

2,3:4,5-*Di*-O-*methylenegalactaroyl Dichloride*.—Finely powdered, anhydrous di-*O*-methylenegalactaric acid[6] (10 g.) was refluxed for 6 hr. with thionyl chloride (50 ml.), the excess of thionyl chloride removed *in vacuo*, and the crystalline acid chloride washed with light petroleum (b. p. 60—80°; 50 ml.) and stored over phosphoric oxide. The compound (11·06 g., 95%) had m. p. 72°, identical with that recorded by Butler, Lawrance, and Stacey[6] (Found: C, 35·5; H, 3·1; Cl, 26·0. Calc. for $C_8H_8Cl_2O_6$: C, 35·4; H, 2·97; Cl, 26·15%). The acid chloride recrystallises from light petroleum (b. p. 60—80°), but this effects no further purification when purity is determined by the viscosity of the polyamide formed with hexamethylenediamine. Carbon tetrachloride was the solvent used in polycondensations.

Dimethyl 2,4:3,5-*Di*-O-*methylene*-D-*glucarate*.—This ester was originally prepared[15] in 18% yield. The following procedure gave twice the yield. Potassium hydrogen D-glucarate (52·5 g.) was refluxed with stirring for 5 days with dry methanol (200 ml.) containing sulphuric acid (9·5 ml.). The mixture was filtered, the filtrate cautiously evaporated to remove methanol,

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[13] Haworth and Wiggins, *J.*, 1944, 58.

[14] Hann and Hudson, *J. Amer. Chem. Soc.*, 1945, **67**, 602.

[15] Haworth, Jones, Stacey, and Wiggins, *J.*, 1944, 61.

and the thick syrup heated at 80° for 90 min. with paraformaldehyde (40 g.) and sulphuric acid (16 ml.). The mixture was refluxed with dry methanol (250 ml.) for 6 hr., and the filtrate crystallised at 0° for 4 days. The crystals (31·5 g.) were extracted with cold chloroform (2 × 300 ml.), the extracts concentrated, and the residue (23·8 g.) was recrystallised from methanol to give the pure ester (19·7 g., 36%), m. p. 157°, $[\alpha]_D$ +33·3° (*c* 2 in $CHCl_3$).

2,4:3,5-*Di*-O-*methylene*-D-*glucaroyl Dichloride.*—Finely powdered, anhydrous di-*O*-methylene-D-glucaric acid [15] (5 g.) was treated with thionyl chloride, as described above, and the crude acid chloride refluxed with dry carbon tetrachloride (300 ml.); the solution was filtered and concentrated to a syrup which crystallised. The crystals were washed with light petroleum to yield 2,4:3,5-*di*-O-*methylene*-D-*glucaroyl dichloride* (4·90 g., 85%), m. p. 70°, $[\alpha]_D$ +73·5° (*c* 1 in benzene), +66·5° (*c* 0·5 in *m*-cresol) (Found: C, 35·7; H, 3·1; Cl, 26·1%). A solution in carbon tetrachloride was used in polycondensations.

2,4:3,5-*Di*-O-*methylene*-L-*idaroyl Dichloride.*—Finely powdered, recrystallised di-*O*-methylene-L-idaric acid [13, 14] (5·01 g.) was refluxed with thionyl chloride (100 ml.) for 5 hr., the mixture cooled, dimethoxyethane (100 ml.) added with cooling, and refluxing continued until the acid had dissolved (2—4 hr.). The hot solution was filtered and cooled to 0°, to give the crystalline *diacid dichloride* (4·49 g., 77%), m. p. 217—220° (slow heating), $[\alpha]_D$ +135° (*c* 0·2 in benzene), +143° (*c* 0·5 in *m*-cresol) (Found: C, 35·5; H, 3·3; Cl, 26·0%). The compound recrystallised from benzene (100 vols.) but no further purification resulted. It was almost insoluble in carbon tetrachloride, and sparingly soluble in methylene chloride, benzene, and chloroform. A 1·1% w/v solution in methylene chloride was used in polycondensations.

2,3,4,5-*Tetra*-O-*acetylgalactaroyl Dichloride.*—Tetra-*O*-acetylgalactaric acid [2] (6 g.) was refluxed at 65—70° for 6 hr. with thionyl chloride (36 ml.) and acetyl chloride (50 ml.). The hot mixture was filtered to remove undissolved acid (36·6%), and then cooled to 0°, to give crystalline tetra-*O*-acetylgalactaroyl dichloride (2·83 g., 68% after allowance for undissolved acid), m. p. 176—178° (Found: C, 40·4; H, 3·97; Cl, 17·0. Calc. for $C_{14}H_{16}Cl_2O_{10}$: C, 40·5; H, 3·89; Cl, 17·1%). In our hands, this method gave a purer compound than that obtained by earlier methods.[2, 16] Carbon tetrachloride and chloroform were used as solvents.

General Procedure for the Preparation of Polyamides by Interfacial Polycondensation.—The "stirred interfacial polycondensation technique" of Beaman and his co-workers [10] was used. The acid dichloride (3 mmoles), in a water-immiscible solvent (carbon tetrachloride except where otherwise stated) (50 ml.), was added to a cold (0°) solution of the diamine (3 mmoles) in 0·2N-sodium hydroxide (30 ml.; 6 mmoles), and the solutions were mixed in a high-speed macerator (Townson and Mercer Ltd.). With the carbohydrate diamine dihydrochlorides, 0·4N-sodium hydroxide (30 ml., 12 mmoles) was added to liberate the free diamine in the aqueous phase. Mixing was continued for 5 min., or for longer periods in some preparations. With hexamethylenediamine and the carbohydrate diacid chlorides, a mixing period of 5 min. was sufficient, but with the carbohydrate diamines and sebacoyl dichloride longer periods were required for optimum yields. This effect was very marked in the preparation of polymer from diaminodimethylenemannitol, but less noticeable with diaminodimethylenegalactitol. Polyamides were washed with 0·1N-hydrochloric acid, 0·1N-sodium hydroxide, water, ethanol, and ether, and dried over phosphoric oxide at 20°/0·5 mm. This general procedure could be scaled up satisfactorily to allow the preparation of 20 g. or more of polymer in a single experiment.

Poly-(1,6-*dideoxy* - 2,3:4,5 - *di*- O - *isopropylidene* - 1 - *sebacamidogalactitol*). —A solution of sebacoyl dichloride (3·467 g., 14·5 mmoles) in carbon tetrachloride (230 ml.) at 0° was added to a cold solution of diaminodi-isopropylidenegalactitol (3·775 g., 14·5 mmoles) in 0·2N-sodium hydroxide (145 ml., 29 mmoles), and the solutions were mixed in a macerator for 5 min. The polymer was washed with 0·01N-hydrochloric acid, 0·1N-sodium hydroxide, and water, the crude product extracted with boiling ethanol (115 ml.) and the extract poured into dilute sodium chloride solution (2 l.). The precipitate was washed with water, to give *poly*-(1,6-*dideoxy*-2,3:4,5-*di*-O-*isopropylidene*-1-*sebacamidogalactitol*) as a white, fibrous polymer (3·903 g., 63%).

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[16] Müller, *Ber.*, 1914, **47**, 2654.