268. *Sugar Osazones and their Anhydrides.*

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This paper deals with further investigations on the production of anhydro-osazones by the deacetylation of osazone acetates. A monoanhydro-lactosazone and two isomeric monoanhydro-maltosazones are described, all of which yield penta-acetates and therefore possess a pyranose ring structure in addition to the pyrazolidine or pyridazine ring. The monoanhydro-glucosazone and -galactosazone described by Diels and his co-workers also appear to contain an oxide ring, since they yield diacetates on acetylation.

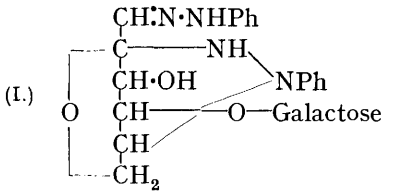
It is pointed out as a result of further work on the differential deacetylation of osazone acetates that this titration method cannot be used as evidence of the cyclic structure or otherwise of such derivatives.

It was shown by one of us (J., 1936, 1770) that the deacetylation of the acetyl derivatives of glucosephenylosazone and galactosephenylosazone gave rise to the same dianhydro-hexosazone, for which a structure was proposed incorporating a pyrazoline, a pyrazolidine, and a pyranose ring. Previously Diels and Meyer (*Annalen*, 1935, **519**, 157) and later Diels, Meyer, and Onnen (*ibid.*, 1936, **525**, 94) had reported the isolation of monoanhydro-glucosazone, -galactosazone, -lactosazone, -xylosazone, -arabinosazone, -cellobiosazone, dianhydro-maltosazone and other similar derivatives by the action of sulphuric acid in alcoholic solution on the osazones. Emil Fischer in his classical paper on osazone formation (*Ber.*, 1887, **20**, 830) had also reported the isolation of anhydrolactosazone by this method.

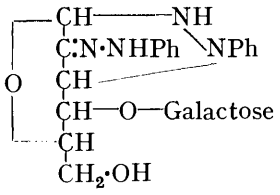
We have now investigated further the possibility of anhydride formation in the sugar osazone series by the deacetylation method for the acetates of the phenylosazones of lactose, maltose, *d*-xylose, *l*-arabinose, and *l*-rhamnose, as well as for certain phenylhydrazones and methylphenylhydrazones, but positive results have been obtained only in the case of the first two substances.

Lactosazone yields an amorphous *hepta-acetate*, which on deacetylation reverts to the same anhydro-derivative (m. p. 232°) as that described by Fischer and by Diels and Meyer (*locc. cit.*). Ultimate analysis reveals the fact that the formula must be represented as $C_{24}H_{32}O_9N_4$, and since it is not identical with lactosazone it appears to be a hydrated anhydride. The corresponding acetyl derivative crystallises with one molecule of benzene and appears to be a *penta-acetyl monoanhydrolactosazone*, the analytical figures not being in agreement with those required by a dianhydrolactosazone tetra- or penta-acetate, or by monoanhydrolactosazone hexa-acetate. It is probable, therefore, that a pyranose ring

structure is present in this monoanhydrolactosazone and it can accordingly be formulated as either (I) or (II).



(I.)



(II.)

It should be noted that the above formulæ are not stereochemical.

Crystalline *maltosazone hepta-acetate* gave two distinct products on deacetylation: (A) $C_{24}H_{30}O_8N_4$, long, lemon-yellow needles, m. p. 245°, $[\alpha]_D^{20°}$ + 57·6° in pyridine (*c*, 0·38), and (B) $C_{24}H_{34}O_{10}N_4$, pointed, yellow plates, m. p. 194°, $[\alpha]_D^{20°}$ + 160° in pyridine (*c*, 0·23). Since by no method of dehydration or hydration attempted was it possible to interconvert (A) and (B), coupled with the evidence of the specific rotations, it is necessary to conclude that the two derivatives are structurally different. The possibility too that (B) is maltosazone hydrate can be ruled out on the basis of the rotational evidence and the fact that on acetylation (B) yields a *penta-acetate*, $C_{34}H_{40}O_{13}N_4$, and not maltosazone hepta-acetate. Acetylation of (A) also yields an amorphous *penta-acetate* of the same composition but with properties markedly different from those of acetylated (B). The simplest explanation available is that (A) and (B) are the isomeric ring forms corresponding to formulæ (I) and (II) suggested for the anhydrolactosazone, but it has not yet been found possible to distinguish between the two forms. It is interesting to note that, although by the deacetylation method glucosazone yields a dianhydrohexosazone and maltosazone and lactosazone monoanhydrides, yet Diels and Meyer (*loc. cit.*) by their method obtained a monoanhydroglucosazone and a dianhydromaltosazone.

In a paper (J., 1935, 1398) a structure for glucosazone was proposed embodying a fructopyranose ring on the basis of methylation experiments. There seems to be no reason why this should not hold for the anhydro-osazones of the disaccharides now considered, but since no experimental proof is yet available for these derivatives it is necessary to suspend judgment on the location of the oxide ring which is undoubtedly present.

The *triacetates* of *d*-xylosazone, *l*-arabinosazone and *l*-rhamnosazone were prepared, but despite repeated attempts crystalline anhydro-osazones could not be obtained by the deacetylation method, although Diels, Meyer, and Onnen (*loc. cit.*) found it possible with acidified alcohol to prepare monoanhydrides of xylosazone and arabinosazone.

Since all the osazone anhydrides prepared by deacetylation appeared to possess an oxide ring structure, it seemed of interest to investigate whether the monoanhydrides of Diels were of the same type. Accordingly his monoanhydro-glucosazone and -galactosazone were prepared and acetylated. The former yielded an amorphous *diacetate*, $[\alpha]_D^{17°}$ — 125°, and a crystalline *diacetyl monoanhydrogalactosazone*, $[\alpha]_D^{17°}$ + 64°, was also isolated. These results would suggest that these monoanhydrides possess an oxide ring structure. This is supported by the observation of Diels, Meyer, and Onnen (*loc. cit.*) that they yield dibenzoates, but these authors also report the isolation of triacetates. The latter observation may be due to acetylation on one of the nitrogen atoms of the hydrazone residue due to the employment of vigorous methods of acetylation. No specific rotations were recorded for these derivatives.

Fructosemethylphenylosazone tetra-acetate on deacetylation yielded the original osazone as would be expected, since no α-hydrogen atom is available for anhydride formation; Diels and Meyer (*loc. cit.*) record a similar observation for their acid alcohol method. Incidental to the preparation of fructosemethylphenylosazone a compound which appears to be a *fructosemethylphenylhydrazone*, m. p. 170°, $[\alpha]_D^{17°}$ — 253°, yielding a *penta-acetate*, m. p. 121°, $[\alpha]_D^{17°}$ + 86·5°, was isolated. Ofner (*Monatsh.*, 1905, **26**, 1165) has described a fructosemethylphenylhydrazone of m. p. 116—120°. It was not found possible to isolate an anhydro-compound from the acetate of glucosephenylhydrazone or from *glucosemethylphenylhydrazone penta-acetate*.

Because of the importance of being able to distinguish between *O*-acetyl and *N*-acetyl groups in this work and because the results in a previous paper (Percival, *loc. cit.*) did not agree with those of Wolfrom, Konigsberg, and Soltzberg (*J. Amer. Chem. Soc.*, 1936, **58**, 490) an extensive survey of the method previously described has been carried out. Repetition of the work on tetra-acetyl galactosazone and tetra-acetyl glucosazone with the conditions of temperature prescribed by Kunz and Hudson (*J. Amer. Chem. Soc.*, 1926, **48**, 1982) indicated the presence of *ca.* 30—31% of *O*-acetyl group, and we are now in complete agreement with Wolfrom and his co-workers on the experimental facts. The reason for the discrepancy was the inaccuracy below 0° of the thermometer used for registering the temperature of the freezing mixture, with the result that the earlier experiments had been conducted at — 15° to — 18° instead of *ca.* — 5°. Whereas at the lower temperature results were obtained, and these are now confirmed, corresponding to the removal of but three acetyl residues, it is apparent that the speed of deacetylation under these conditions will be much reduced, and experiments with octa-acetyl lactose reveal that, although 20 minutes at room temperature is sufficient to eliminate all the acetyl residues, at — 20° only about 90% is removed in 2 hours, so that the agreement may be fortuitous. It must be emphasised, however, that it does not follow that the compounds in question do not contain *N*-acetyl groups, and are therefore acyclic. It is clear that it is not sufficient to compare *O*-acetylated compounds with such derivatives as acetanilide and methylacetanilide, which are untouched during 24 hours with *N*/10-sodium hydroxide at room temperature, since the compounds under review, if cyclic, will be acetylated hydrazides. Accordingly the ease of deacetylation of α-acetylphenylhydrazine, β-acetylphenylhydrazine, αβ-diacetylphenylhydrazine and benzaldehyde-α-acetylphenylhydrazone was studied. The general conclusion emerges that such compounds are hydrolysed much more easily than *N*-acetylated amines, but to a varying extent; *e.g.*, β-acetylphenylhydrazine requires but 2 hours at room temperature under the prescribed conditions to lose 50% of its acetyl residues and diacetylphenylhydrazine loses almost the same proportion in 10 minutes, although benzaldehyde-α-acetylphenylhydrazone only loses 13% and α-acetylphenylhydrazine 7% in 2 hours. It is therefore clear that a sharp differentiation between NH·NAc and OAc is difficult by the method proposed and that the question of the structure of the osazone acetates cannot yet be regarded as settled.

Experimental.

Acetylation of Lactosephenylosazone.—The method described for the acetylation of dianhydrohexosazone (J., 1936, 1773) was employed, giving, in almost quantitative yield, an amorphous yellow powder, which was washed, dried, dissolved in benzene, and precipitated with light petroleum (b. p. 40—60°) to yield a pale yellow solid, m. p. 105—110°, $[\alpha]_D^{20°}$ + 27° in chloroform (*c*, 0·28) (Found: C, 56·6; H, 5·6; CH_3·CO, 35·7; N, 7·1. $C_{38}H_{46}O_{16}N_4$ requires C, 56·0; H, 5·65; CH_3·CO, 37·0; N, 6·9%).

Conversion into Anhydrolactosephenylosazone.—Hepta-acetyl lactosephenylosazone (4 g.), dissolved in acetone (180 c.c.) and water (100 c.c.), was mixed with sodium hydroxide solution (44 c.c., 8%) at room temperature and kept for 21 hours. The resulting solution was neutralised with sulphuric acid and diluted with acetone until the precipitation of sodium sulphate was complete. This was removed by filtration, and the acetone by distillation. Yellow needles were deposited, which were filtered off from the hot solution; a further quantity of needles was deposited from the filtrate on standing. Recrystallisation from hot pyridine–alcohol, followed by the addition of water, gave light yellow, fan-like needles (1 g.), m. p. 231—232° (not depressed by Diels's anhydrolactosazone, m. p. 230°), $[\alpha]_D^{20°}$ — 147° in methyl alcohol (*c*, 0·18) (cf. Diels's anhydrolactosazone, $[\alpha]_D^{20°}$ — 146° in methyl alcohol; *c*, 0·19) (Found: C, 55·2; H, 6·1; N, 11·6. Calc. for $C_{24}H_{32}O_9N_4$: C, 55·4; H, 6·2; N, 10·8%).

Preparation of Anhydrolactosephenylosazone Penta-acetate.—Anhydrolactosephenylosazone (0·4 g.) was acetylated as described for the acetylation of lactosephenylosazone. On pouring into water a yellow precipitate was obtained. Rosettes of shining yellow needles were obtained by solution in warm benzene, followed by the addition of light petroleum (b. p. 40—60°) until turbidity was almost reached (yield 0·5 g.); m. p. 115—117°, $[\alpha]_D^{20°}$ — 102° in acetone (*c*, 0·4) [Found: C, 60·3; H, 5·82; CH_3·CO, 29·0 (titrn.), 28·0 (Freudenberg); N, 7·1. $C_{40}H_{46}O_{13}N_4$ requires C, 60·7; H, 5·9; CH_3·CO, 27·3; N, 7·1%]. Deacetylation of the *penta-acetate* gave the original anhydrolactosazone, m. p. 232°, $[\alpha]_D^{17°}$ — 147° in methyl alcohol (*c*, 0·2).

Acetylation of Maltosephenylosazone.—Maltosephenylosazone was acetylated as described above for lactosephenylosazone. The *product*, obtained in quantitative yield, was recrystallised from alcohol and water to yield rosettes of yellow needles, m. p. 162°, $[\alpha]_D^{20°}$ + 41° in chloroform (*c*, 0·515) (Found: C, 55·7; H, 5·6; CH_3·CO, 37·0; N, 6·8. $C_{38}H_{46}O_6N_4$ requires C, 56·0; H, 5·65; CH_3·CO, 37·0; N, 6·9%).

Preparation of Anhydromaltosephenylosazone.—Hepta-acetyl maltosephenylosazone (9·5 g.) was deacetylated as described above for hepta-acetyl lactosephenylosazone. A yellow precipitate (A) was again deposited in the hot solution and a further quantity of precipitate (B) in the filtrate on standing. The precipitate (A) was recrystallised in the same way as the lactose compound to give long, pale yellow needles (0·3 g.), m. p. 245—246°, mixed m. p. with anhydroglucosephenylosazone (m. p. 230—232°) 224—226°; $[\alpha]_D^{20°}$ + 58° in pyridine (*c*, 0·382) (Found: C, 57·6; H, 6·0; N, 10·9. $C_{24}H_{30}O_8N_4$ requires C, 57·4; H, 6·0; N, 11·2%).

The precipitate (B) was similarly treated to yield bright yellow, pointed plates mixed with a small quantity of the light yellow needles (0·05 g.). It was found that the needles were deposited while the recrystallisation solution was warm and separation was effected by filtration of the hot solution. Any plates adhering to the needles could be removed by washing with alcohol. The addition of a further quantity of water was sometimes necessary to ensure complete deposition of the plates (2·3 g.), m. p. 194°; mixed m. p. with maltosephenylosazone (m. p. 196—199°) 165°; $[\alpha]_D^{20°}$ + 160° in pyridine (*c*, 0·23), + 90° in methyl alcohol (*c*, 0·552), + 92° in 6 : 4 alcohol–pyridine (*c*, 0·3) (Found: C, 53·6; H, 6·3; N, 10·7. $C_{24}H_{34}O_{10}N_4$ requires C, 53·5; H, 6·3; N, 10·4%).

Acetylation of Anhydromaltosephenylosazone.—(a) *Needle form.* The needles (0·27 g.) were acetylated as described above, slight warming being necessary to obtain solution of the crystals. On pouring into water an orange-red precipitate was obtained, which defied all attempts at crystallisation. The best method of purification was solution in benzene, followed by precipitation with light petroleum (b. p. 60—80°) to give a pale fawn, amorphous *penta-acetate* (0·4 g.), $[\alpha]_D^{20°}$ + 90·7° in acetone (*c*, 0·275) [Found: C, 56·7; H, 5·6; CH_3·CO (Freudenberg), 30·0; N, 7·3. $C_{34}H_{40}O_{13}N_4$ requires C, 57·3; H, 5·6; CH_3·CO, 30·2; N, 7·9%]. All attempts to obtain a crystalline anhydro-compound or to regenerate the original material by deacetylation of the above acetate failed.

(b) *Plate form.* The plates (1·3 g.) were acetylated as described above to yield a pale yellow solid. Recrystallisation from alcohol gave an amorphous *penta-acetate* (1·8 g.), m. p. 110—112°, $[\alpha]_D^{20°}$ + 150° in acetone (*c*, 0·29) [Found: C, 56·8; H, 5·5; CH_3·CO, 30·5 (titrn.), 30·8 (Freudenberg); N, 7·5. $C_{34}H_{40}O_{13}N_4$ requires C, 57·3; H, 5·6; CH_3·CO, 30·2; N, 7·9%]. Deacetylation of the above acetate (1 g.) and treatment in the usual manner gave the original pure plates (0·25 g.), m. p. 194°, $[\alpha]_D^{18°}$ + 160° in pyridine (*c*, 0·243).

d-*Xylosazone Triacetate*, l-*Arabinosazone Triacetate, and* l-*Rhamnosazone Triacetate.*—The pure osazone (1 g.) was dissolved in pyridine (5·5 c.c.) and acetic anhydride (2 c.c.) and kept for 36 hours. The solid obtained on pouring into water was recrystallised from aqueous ethyl alcohol.

d-*Xylosazone triacetate* crystallised in clumps of needles, m. p. 116—117°, $[\alpha]_D^{16°}$ − 46° in chloroform (*c*, 0·3) [Found: C, 60·9; H, 5·9; CH_3·CO, 29·9 (Freudenberg), 27·9 (titrn.); N, 12·7. $C_{23}H_{26}O_6N_4$ requires C, 60·7; H, 5·8; CH_3·CO, 28·4; N, 12·3%].

l-*Arabinosazone triacetate* was similar in appearance to the corresponding xylose derivative; it had m. p. 114°, $[\alpha]_D^{16°}$ *ca.* + 5° in chloroform (*c*, 0·3) [Found: C, 61·2; H, 6·1; CH_3·CO, 30·0 (Freudenberg), 28·0 (titrn.); N, 12·5. $C_{23}H_{26}O_6N_4$ requires C, 60·7; H, 5·8; CH_3·CO, 28·4; N, 12·3%].

l-*Rhamnosazone triacetate* was obtained as an amorphous yellow solid, m. p. 75°, $[\alpha]_D^{18°}$ + 52° in chloroform (*c*, 0·4) [Found: C, 61·4; H, 6·0; CH_3·CO (titrn.), 28·4; N, 12·2. $C_{24}H_{28}O_6N_4$ requires C, 61·5; H, 6·0; CH_3·CO, 27·6; N, 12·0%].

Deacetylation of these compounds according to the conditions previously described gave ill-defined brownish-yellow solids which could not be obtained crystalline.

Monoanhydroglucosazone and Monoanhydrogalactosazone Diacetates.—Diels and Meyer's method (*loc. cit.*) was used to prepare monoanhydroglucosazone, m. p. 177°, $[\alpha]_D^{17°}$ − 154° in methyl alcohol (*c*, 0·45) (Found: C, 63·2; H, 6·1; N, 16·3. Calc. for $C_{18}H_{20}O_3N_4$: C, 63·5; H, 5·9; N, 16·5%), and monoanhydrogalactosazone, m. p. 217°, $[\alpha]_D^{20°}$ + 28° in methyl alcohol (*c*, 0·3) (Found: C, 63·1; H, 6·0; N, 16·2. Calc. for $C_{18}H_{20}O_3N_4$: C, 63·5; H, 5·9; N, 16·5%). Both these derivatives (1 g.) were acetylated with pyridine (8 c.c.) and acetic anhydride (3·5 c.c.) during 3 days at room temperature and the acetates were isolated by pouring into water. *Monoanhydroglucosazone diacetate* was obtained as a yellow amorphous powder, m. p. 70°,

$[\alpha]_D^{17°}$ — 125° in chloroform (*c*, 0·3) [Found: C, 62·0; H, 5·8; CH_3·CO, 21·2 (Freudenberg), 21·4 (titrn.); N, 12·8. $C_{22}H_{24}O_5N_4$ requires C, 62·3; H, 5·7; CH_3·CO, 20·3; N, 13·2%]. *Monoanhydrogalactosazone diacetate* crystallised in yellow needles, m. p. 86°, $[\alpha]_D^{18°}$ + 64° in chloroform (*c*, 0·2) [Found: C, 61·9; H, 5·8; CH_3·CO, 21·6 (Freudenberg), 21·0 (titrn.); N, 13·5. $C_{22}H_{24}O_5N_4$ requires C, 62·3; H, 5·7; CH_3·CO, 20·3; N, 13·2%].

Fructosemethylphenylosazone Tetra-acetate.—The instructions of Ofner (*Ber.*, 1904, **37**, 3362) were followed, but the product was invariably the *methylphenylhydrazone* described below. Neuberg's method (*Ber.*, 1902, **35**, 959), however, gave the methylphenylosazone, m. p. 156°, $[\alpha]_D^{17°}$ + 90° in pyridine–alcohol (4 : 6) (*c*, 0·4). Acetylation according to the usual method gave a yellow crystalline acetate in quantitative yield, m. p. 128°, $[\alpha]_D^{17°}$ — 435° in chloroform (*c*, 0·4), — 236° in 95% alcohol (*c*, 0·2) (cf. Engel, *J. Amer. Chem. Soc.*, 1935, **57**, 2419) (Found: C, 60·9; H, 6·2; CH_3·CO, 30·9; N, 10·0. Calc. for $C_{28}H_{34}O_8N_4$: C, 60·6; H, 6·2; CH_3·CO, 31·0; N, 10·1%).

Fructosemethylphenylhydrazone.—Ofner's method (*loc. cit.*) for the preparation of the osazone readily gave a colourless crystalline derivative, which on recrystallisation yielded prisms, m. p. 170°, $[\alpha]_D^{17°}$ — 253° in pyridine–alcohol (4 : 6) (*c*, 0·6) (Found: N, 10·3. $C_{13}H_{20}O_5N_2$ requires N, 9·9%).

Fructosemethylphenylhydrazone Penta-acetate.—The methylphenylhydrazone (1 g.) was kept with acetic anhydride (3 c.c.) and pyridine (6 c.c.); after 2 days the mixture was poured into water, and the solid recrystallised from 50% aqueous alcohol to yield colourless plates of the *penta-acetate*, m. p. 121°, $[\alpha]_D^{17°}$ + 86·5° in chloroform (*c*, 0·9) (Found: C, 56·0; H, 6·1; CH_3·CO, 42·8; N, 6·4. $C_{23}H_{30}O_{10}N_2$ requires C, 55·85; H, 6·1; CH_3·CO, 43·5; N, 5·7%).

Substance.	Temp.	Time (hrs.).	% CH_3·CO.
Galactosazone tetra-acetate (32·5)	−22°	0·5	22·2
	−22	1·33	21·2
	−20 → −14	2·0	23·0
	−20 → −18	2·33	25·0*
	−20 → −10	3·17	26·6
	−23 → −21	3·5	28·3
	−20 → −17	4·0	27·4
	−20 → −18	6·42	29·0
	− 4 → − 6	2·0	29·9*
	− 4 → − 6	3·0	31·9
	+ 17	2·0	33·4*
	+ 17	2·67	34·0
	+ 17	3·0	33·6
	+ 17	4·0	33·5*
Lactose octa-acetate (50·0)	−19 → −18	0·2	24·4
	−19 → −18	0·45	30·0
	−19 → −18	0·83	42·9
	−19 → −18	1·5	43·0
	−19 → −18	2·0	45·9
	−20 → −17	4·67	48·9
	+ 16	0·02	28·0
	+ 16	0·08	39·3
	+ 16	0·25	47·3
	+ 16	4·0	49·2*
Acetanilide (31·9)	+ 18	24·0	0
Methylacetanilide (28·9)	+ 18	24·0	0
Fructosemethylphenylosazone tetra-acetate (31·0)	−19	2·0	27·0
	−10	2·0	30·8
Fructosemethylphenylhydrazone penta-acetate (43·5)	−19	2·0	38·0
	− 5 → + 2	2·5	42·8
Xylosazone tri-acetate (28·4)	−12	2·0	18·0
	+17	2·0	26·0
Arabinosazone tri-acetate (28·4)	−13 → −10	2·0	20·0
	+17	2·0	28·0
" Dianhydro-hexosazone " mono-acetate (11·8)	−20°	2·0	7·0
	−10	2·0	9·0
	+17	7·0	11·9
Lactosazone hepta-acetate (37·0)	−20	2·0	24·1
	+17	2·0	36·0
Maltosazone hepta-acetate (37·0)	−10	2·0	32·0
	+16	2·0	37·0
	+16	4·0	37·3
Glucosephenylhydrazone penta-acetate (44·8)	−10 → −15	2·0	32·0
	+16	3·0	43·4
Glucosemethylphenylhydrazone penta-acetate (43·6)	−17 → −14	0·5	22·3
	−17 → −14	1·0	34·6
	−17 → −14	2·0	37·9
	−17 → −10	4·0	39·8
	−17 → − 8	6·5	42·3
	− 0 → − 5	14·0	40·5
	+16	3·0	43·1
β-Acetylphenylhydrazine (28·7)	−20	2·0	8·0
	−4 → 0	2·0	9·0
	+17	2·0	14·0
	+17	5·0	22·7
	+17	17·0	24·5
α-Acetylphenylhydrazine (28·7)	+16	2·0	1·7
	+16	18·0	8·0
	+16	47·0	18·0
αβ-Diacetylphenylhydrazine (44·7)	−17 → −14	2·0	19·9
	+17	0·08	17·0
	+17	0·16	20·5
	+17	0·5	20·8
	+17	3·5	21·0
	+17	4·0	24·2
	+17	21·0	33·7
	+17	42·0	41·1
Benzaldehyde-α-acetylphenylhydrazone (18·1)	+17	2·0	2·3
	+17	20·0	13·0

Glucosephenylhydrazone Penta-acetate.—This derivative was prepared from glucosephenylhydrazone, m. p. 159°, $[\alpha]_D$ — 82° in water (*c*, 0·5), by the method of Behrend and Reinsberg

(*Annalen*, 1910, **377**, 189). The needles had m. p. 152°, $[\alpha]_D^{17°}$ — 10·4° in pyridine (*c*, 0·5) (Found : CH_3·CO, 43·4; N, 6·0. Calc. for $C_{22}H_{28}O_{10}N_2$: CH_3·CO, 44·8; N, 5·8%).

Glucosemethylphenylhydrazone Penta-acetate.—Glucosemethylphenylhydrazone (m. p. 131°; 3 g.) prepared according to the method of Ofner (*loc. cit.*) was acetylated by the addition of acetic anhydride (6 c.c.) and pyridine (16 c.c.) during 45 minutes with constant stirring; after 12 hours the mixture was poured into cold water. The white gummy solid obtained gave, on recrystallisation from alcohol, white shining prisms of the *penta-acetate* (2·5 g.), m. p. 113—114°, $[\alpha]_D$ + 157° in chloroform (*c*, 0·5) (Found : CH_3·CO, 43·1; N, 5·9. $C_{23}H_{30}O_{10}N_2$ requires CH_3·CO, 43·6; N, 5·7%).

Acetyl Estimations by Direct Titration.—For these experiments 0·10—0·15 g. of material was dissolved in acetone (35 c.c.), *N*/10-sodium hydroxide (25 c.c.) added, drop by drop in the case of the experiments in the cold, and the solution, after dilution, back-titrated with *N*/10-sulphuric acid and phenol-red. Controls were carried out on the acetone used in each experiment. Experiments using the quinhydrone electrode gave almost identical results in the cases marked *. The theoretical percentage of acetyl in each compound is given in parentheses after the name in the table.

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