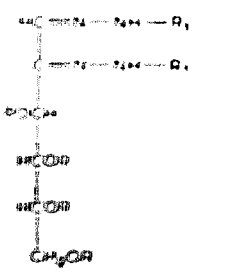
**Preliminary Communication**

# Carbohydrate derivatives of 1-substituted 1,2,3-triazole

Recently, Curtin and Alexandrou[1] have studied the structure of the oxidation products obtained by the action of iodine and mercuric oxide on the bis(benzoylhydrazones) of dimethylglyoxal, pyruvaldehyde, and benzil. They found that the products possessed ester bands at 1750 $cm^{-1}$ but not the amide band that would be expected on the basis of the tetrazine structures previously[2] ascribed to them. This fact and other experiments led the authors to consider these compounds to be derivatives of 1-benzoylamino-1,2,3-triazole enol benzoate.

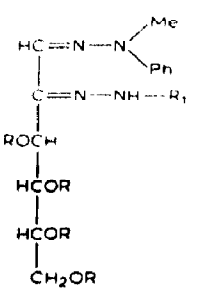
For a similar oxidation in the carbohydrate series, the D-*arabino*-hexosulose bis(acylhydrazones) (Ia) shown in the Table were prepared from D-*arabino*-hexosulose (glucosone) and acyl hydrazines, by the procedure used for the prepration of carbamoyl osazones[3]. The colorless bis(acylhydrazones) obtained showed two CONH bands between 1640–1690 $cm^{-1}$, in addition to a C=N band which appeared between 1595–1615 $cm^{-1}$ (see Table I).

Acetylation of the bis(acylhydrazones) gave the tetraacetates (Ib) which showed, in addition to the amide bands, an ester band at 1750 $cm^{-1}$. Oxidation of these acetyl derivatives with iodine and mercuric oxide gave products (III) having two hydrogen atoms fewer than the bis(acylhydrazone) acetates.

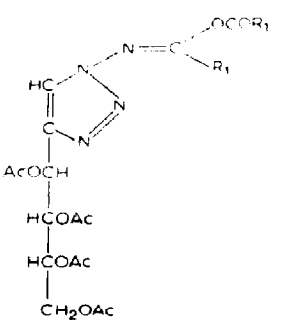


(I)

a, B = H; b, B = Ac




(II)




(III)

The i.r. spectra of the oxidation products revealed no CONH bands but showed large ester bands at 1750 $cm^{-1}$ (see Table) probably arising from the *O*-acetyl and the

TABLE I[a]

BIS(ACYLHYDRAZONE) DERIVATIVES

| *Formula* $R_1$ | *M.p., degrees* | *Color* | *Yield, %* | $[\alpha]_D$ (°) | $\nu_{max}^{KBr}$ | | | $\lambda^{EtOH}$ | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | $\nu_{C=N}$ | $\nu_{CONH}$ | $\nu_{OH}$ | $\lambda_{max}$ | log ε | $\lambda_{min}$ | log ε |
| Ia –$SCNH_2$ | 232 | Yellow | 60 | −27.2 (P) | 1612 | [b] | 3220 | [c] | [c] | [c] | [c] |
| Ia –OCNHPh | 245 | Pale yellow | 55 | −114.9 (P) | 1600 | 1640, 1665 | 3300 | [c] | [c] | [c] | [c] |
| Ia –OCMe | 216 | Colorless | 60 | −18.1 (W) | 1610 | 1675, 1695 | 3290 | 296 | 4.49 | 225 | 3.62 |
| Ia –OCpyridyl-3 | 202 | Colorless | 50 | −52.8 (P) | 1595 | 1665, 1685 | 3360 | 251, 320 | 1.87, 4.36 | 217, 286 | 3.86, 4.18 |
| Ia –OCPh | 188 | Colorless | 70 | −89.8 (P) | 1605 | 1665, 1675 | 3450 | 256, 330 | 4.35, 4.24 | 225, 295 | 3.08, 3.97 |
| Ia –$OCC_6H_4Me$-*m* | 167 | Colorless | 70 | −35.0 (A) | 1605 | 1645, 1690 | 3360 | 258, 332 | 4.26, 4.08 | 226, 302 | 3.95, 3.87 |
| Ia –$OCC_6H_4Me$-*p* | 189 | Colorless | 75 | −22.1 (A) | 1610 | 1645, 1690 | 3400 | 262, 332 | 4.40, 4.40 | 230, 298 | 4.23, 4.12 |
| IIa –$OCNH_2$ | 180 | Pale yellow | 45 | −48.2 (P) | 1605 | 1690 | 3280 | 242, 285 | 4.17, 3.64 | 220, 264 | 4.00, 3.64 |
| IIa –$SCNH_2$ | 203 | Yellow | 80 | −27.6 (P) | 1600 | [b] | 3160 | 254, 302 | 4.40, 4.15 | 226, 274 | 4.07, 3.96 |
| IIa –OCMe | 187 | Yellow | 75 | −50.9 (P) | 1600 | 1652 | 3350 | 244, 352 | 3.04, 3.19 | 218, 304 | 2.75, 2.49 |
| IIa –OCpyridyl-3 | 178 | Yellow | 40 | −69.2 (P) | 1598 | 1666 | 3350 | 278, 370 | 4.10, 4.37 | 260, 315 | 4.06, 3.66 |
| IIa –OCpyridyl-4 | 190 | Yellow | 45 | −29.8 (P) | 1595 | 1660 | 3260 | 278, 360 | 4.10, 4.32 | 260, 312 | 4.00, 4.62 |
| IIa –OCPh | 188 | Yellow | 50 | −69.3 (P) | 1600 | 1665 | 3370 | 235, 275 | 4.02, 3.90 | 260, 310 | 3.88, 3.40 |
| IIa –$OCC_6H_4Me$-*o* | 145 | Yellow | 50 | −47.6 (A) | 1600 | 1660 | 3440 | 246, 363 | 4.22, 4.28 | 222, 310 | 4.08, 3.47 |
| IIa –$OCC_6H_4Me$-*p* | 187 | Yellow | 50 | −16.6 (A) | 1610 | 1660 | 3480 | 248, 314 | 4.24, 3.51 | 224, 274 | 4.07, 4.27 |
| | | | | | | | $\nu_{(COO)}$ | | | | |
| Ib –OCPh | 232 | Colorless | 90 | −40.9 (A) | 1605 | 1670, 1690 | 1750 | 256, 336 | 4.42, 4.18 | 226, 298 | 4.15, 3.96 |
| Ib –$OCC_6H_4Me$-*m* | 181 | Colorless | 90 | −40.7 (A) | 1595 | 1675, 1690 | 1750 | 258, 342 | 4.31, 4.13 | 228, 306 | 3.95, 3.84 |
| Ib –$OCC_6H_4Me$-*p* | 153 | Colorless | 90 | −7.8 (A) | 1610 | 1665, 1690 | 1750 | 262, 342 | 4.36, 4.19 | 234, 304 | 4.12, 3.83 |
| IIb –OCMe | 144 | Pale yellow | 80 | −91.0 (A) | 1600 | 1670 | 1750 | 242, 288 | 4.14, 3.63 | 218, 272 | 3.35, 3.61 |
| IIb –OCPh | 132 | Yellow | 90 | −34.2 (A) | 1600 | 1690 | 1750 | 285, 370 | 4.00, 3.98 | 260, 320 | 3.60, 3.40 |
| III –Ph | 198 | Colorless | 20 | −3.7 (P) | 1612 | [d] | 1750 | 255, 315 | 4.10, 4.40 | 235, 268 | 4.00, 4.07 |
| III –$C_6H_4Me$-*m* | 160 | Colorless | 30 | −8.2 (C) | 1614 | [d] | 1750 | 227, 272 | 4.27, 4.00 | 252 | 3.94 |
| III –$C_6H_4Me$-*p* | 169 | Colorless | 30 | −21.8 (C) | 1605 | [d] | 1750 | 232 | 4.36 | 216 | 4.22 |

[a]All compounds gave proper C, H, and N analyses. Specific rotations were determined in: A, ethanol; C, chloroform; P, pyridine; W, water. [b]C=S band at 1500 $cm^{-1}$. [c]Not determined [d]No absorption at this frequency.

enol benzoate groups. These data accord with the general structure of Curtin and Alexandrou[1] for the pyruvaldehyde derivative, and the products are, therefore, tentatively formulated as 4-substituted 1-benzoylamino-1,2,3-triazole enol benzoates (III). The reaction may be exemplified by the conversion of D-*arabino*-hexosulose bis-(benzoylhydrazone) (Ia; $R_1$ = COPh) into the tetraacetate (Ib; $R_1$ = COPh), and the oxidation of the latter to the 1-benzoylamino-4-(D-*arabino*-tetraacetoxybutyl)-1,2,3-triazole enol benzoate (III; $R_1$ = Ph). Mixed osazones of the type (IIa) were also prepared, from D-*arabino*-hexosulose 1-(2-methyl-2-phenylhydrazone) and acylhydrazines. Their acetates (IIb) displayed the expected resistance toward oxidation to enol acylates of the type (III).

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