(singlet, O–CH_3), 5.27 (doublet, J=5.5 Hz, –NH–C<u>H</u>–), 8.64 (doublet, J=5.5 Hz, –N<u>H</u>–CH–), and 9.92 (singlet, COOH). Hydrogenolysis of IIIa with $LiAlH_4$ in tetrahydrofuran gave the corresponding alcohol (V), $C_{29}H_{26}O_3N_2$, mp 135—137°. Its NMR spectrum (in d_6-DMSO) indicated signals at δ 3.72 (singlet, O–CH_3), 4.41 (singlet, –CH_2–O–), 5.74 (broad, O–H), 5.92 (doublet, J=8.0 Hz, NH–C<u>H</u>–), and 8.02 (doublet, J=8.0 Hz, –N<u>H</u>–CH–). The signals at δ 5.74 and 8.02 disappeared on addition of D_2O. Therefore, it was decided that the adduct (IIIa) was 2-(*p*-anisyl)-4-oxo-3,3-diphenyl-2H,3H-pyrimido[2,1-*b*]benzoxazole.

Similarly, the adducts IIIb, IIIc, and VII were obtained from the corresponding azadienes IIb, IIc, and VI, respectively, and the results are summarized in Table I.

Further work on the reaction of diphenylketene with azadienes is in progress.

Table I. Physical Properties of 1,4-Cycloadducts

Product	mp (°C)	Yield (%)	M+ *m/e*	IR ν_{max}^{KBr} cm^{-1} C=O	IR C=N	NMR (in $CDCl_3$) δ C_2–H
IIIb	153—155	87	462	1714	1648	5.45 (1H, s)
IIIc	223—224	81	—	1733, 1681	1614	—
VII	204	87	413	1727	1638	5.47 (1H, s)

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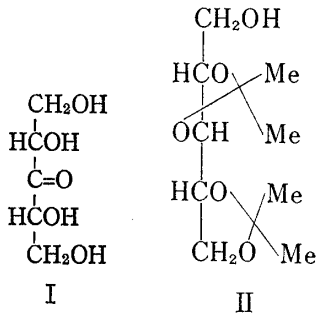
1-Deoxy(2,4-dinitrophenyl)osazones as Characterizing Derivative of 3-Ketoses

In spite of the importance of phenylosazones as characterizing derivatives of sugars, no phenylosazone of 3-ketose has been reported. The attempt of preparing phenylosazone from coriose resulted in recovery of the sugar and production of tarry material upon prolonged warming.[1,2] A crystalline 1-deoxy (2,4-dinitrophenyl)osazone (DNO) was prepared from this 3-heptulose.[2] The synthesis of 3-hexuloses and 3-pentuloses *via* esters and acetals *etc.* have been presented by several workers mostly up to the preparations of these derivatives of 3-ketoses without isolation of 3-ketoses from the hydrolyzates of these derivatives.[3,4] The identification of syrupy 3-ketoses would have been retarded by the difficulties in preparing appropriate crystalline derivatives. It was once suggested upon the attempt of preparing

1) T. Okuda and K. Konishi, *Tetrahedron*, **24**, 6907 (1968).
2) T. Okuda, S. Saito and K. Uobe, *Tetrahedron*, **30**, 1187 (1974).
3) *a*) S.J. Angyal and K. James, *Chem. Comm.*, **1970**, 320; *idem*, *Aust. J. Chem.*, **24**, 1219 (1971); *b*) S.J. Angyal and M.E. Evans, *ibid.*, **25**, 1347, 1495, 1513 (1972); *c*) K.G.A. Jackson and J.K.N. Jones, *Can. J. Chem.*, **47**, 2498 (1969); *d*) A. Sera and R. Goto, *Bull. Chem. Soc. Japan*, **38**, 1415 (1965).
4) A. Sera, *Bull. Chem. Soc. Japan*, **35**, 2033 (1962).

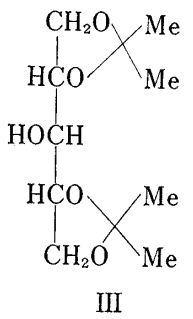
erythro-3-pentulose that the unsubstituted 3-ketose does, in general, not exist in a stable form, but is transformed into isomers by the Lobry de Bruyn transformation.[4] We have now prepared crystalline 1-deoxy (2,4-dinitrophenyl)osazones from syrupy 3-hexuloses and *erythro*-3-pentulose to show that these 3-ketoses are stable upon the hydrolysis, and also that this new type of osazone is applicable to 3-ketoses in general.

In the present work, *erythro*-3-pentulose (I) has been synthesized by DMSO-P_2O_5 oxidation of one of the two diacetonides obtained from xylitol, followed by hydrolysis. While the major diacetonide alcohol II from xylitol, which showed a triplet (DMSO-d_6, δ 4.81, $-CH_2OH$)[5] in the nuclear magnetic resonance (NMR) spectrum, yielded DL-xylose upon DMSO-P_2O_5 oxidation followed by hydrolysis, the minor diacetonide alcohol III, NMR (δ 2.39 d, HCOH), Mass Spectrum M-15 (*m/e* 217), produced a ketone IV which is regarded as 1,2-4,5-diacetonide of I, IR $\nu_{max}^{CHCl_3}$ 1735 cm^{-1} (C=O), NMR (δ 1.37 s 6H, 1.45 s 6H, 4.10 oct 4H, 4.71 dd 2H), M-15 (*m/e* 215), and this ketone was hydrolyzed with 1.5% H_2SO_4–MeOH to give syrupy I, which showed a single spot on paper chromatography (PPC) (*Rf*: A 0.46, B 0.31, C 0.24),[5] and a single peak in gas–liquid chromatography (GLC) of the trimethylsilyl (TMS) derivative (R_{Glu}: a 0.41 (150°), b 0.39 (170°)).[5] The mass spectrum obtained by GC–MS of this TMS derivative was identical with that[6] of I which had been produced as a mixture by the mercuric acetate oxidation of ribitol.[7] The reaction of I with 2,4-dinitrophenylhydrazine in warm 2N HCl

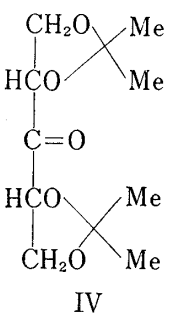


I

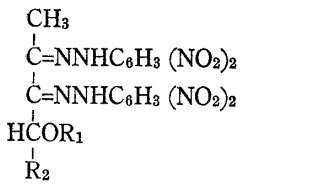
II



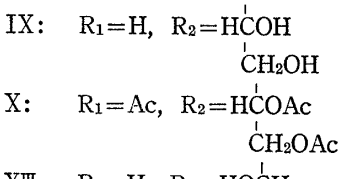
III



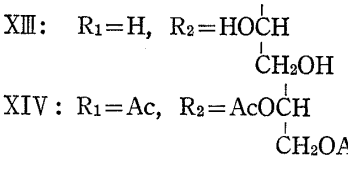
IV



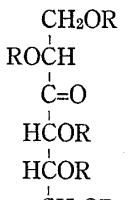
V: R_1=H, R_2=$-CH_2OH$
VI: R_1=Ac, R_2=$-CH_2OAc$



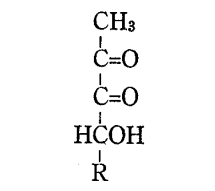
IX: R_1=H, R_2=HCOH, CH_2OH
X: R_1=Ac, R_2=HCOAc, CH_2OAc



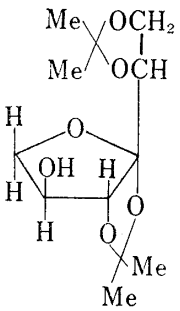
XIII: R_1=H, R_2=HOCH, CH_2OH
XIV: R_1=Ac, R_2=AcOCH, CH_2OAc



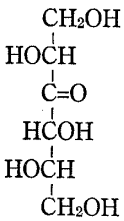
VII: R=Ac
VIII: R=H



XV: R=$-CH_2OH$
XVI: R=HCOH, CH_2OH
XVII: R=HOCH, CH_2OH



XI



XII

5) Unless specified otherwise, NMR spectra were determined in $CDCl_3$ at 90 MHz with tetramethylsilane as the internal standard. PPC was developed ascendingly with (A) *n*-BuOH–C_5H_5N–H_2O, 6:4:3, (B) *n*-BuOH–EtOH–H_2O, 4:1.2:1, and (C) *n*-BuOH–AcOH–H_2O, 4:1:5, and detection was effected by Tollens' reagent and $NaIO_4$-benzidine.[8] GLC was carried out with FID detector on 3 mm × 2 m glass columns containing (a) 1.5% OV-1, (b) 1.5% SE-30 on 80—100 mesh AW-DMCS Chromosorb W. R_{Glu} shows the retention time relative to TMS derivative of α-D-glucose.

6) J. Havlicek, G. Petersson and O. Samuelson, *Acta. Chem. Scand.*, **26**, 2205 (1972).

7) R.J. Stoodley, *Can. J. Chem.*, **39**, 2593 (1961).

for 1 hr yielded an orange-red crystalline product V, $C_{17}H_{16}O_{10}N_8$, mp 237—239°, UV λ_{max}^{EtOH} nm (log ε) 397 (4.59) and 430 (4.58), NMR (C_5D_5N, δ 2.35 s 3H, 4.29 d 2H, 6.13 t). A diacetate VI, $C_{21}H_{20}O_{12}N_8$, mp 143—145°, UV $\lambda_{max}^{CHCl_3}$ nm (log ε) 390 (4.43) and 437 (4.43), NMR (δ 1.94 s 3H, 2.25 s 3H, 2.43 s 3H, 4.56 t 2H, 6.90 q, 7.8—9.3 6H, 11.46 s, 12.73 s), was produced. The large downfield shift of one of the imino protons indicates that a strong chelate ring is formed in analogous way as in 1-deoxycoriose (2,4-dinitrophenyl)osazone.[2]

1,2,4,5,6-O-Pentaacetyl D-*arabino*-3-hexulose (VII)[3b] was hydrolyzed with 1.5% H_2SO_4-MeOH and treated with IR-120 to yield a syrupy sugar VIII, $C_6H_{12}O_6$, $[\alpha]_D^{24}$ −31° (c=2, H_2O), PPC (*Rf*: A 0.47, B 0.34, C 0.25). This sugar gave upon $NaBH_4$ reduction a hexitol mixture which could be regarded as being composed by mannitol and altritol on GLC of TMS derivative although clear resolution was not effected. GC–MS of TMS derivative of VIII showed that this sugar forms an equilibrium mixture.[9] This 3-hexulose yielded DNO IX, $C_{18}H_{18}O_{11}N_8$, mp 185—187°, UV λ_{max}^{EtOH} nm (log ε) 400 (4.73) and 430 (4.71), which was acetylated to give a triacetate X, $C_{24}H_{24}O_{14}N_8$, mp 178°, whose spectra, UV $\lambda_{max}^{CHCl_3}$ nm (log ε) 390 (4.66) and 437 (4.66), NMR (δ 1.96 s 3H, 1.98 s 3H, 2.27 s 3H, 2.44 s 3H, 4.30 oct 2H, 5.69 m, 7.03 d, 7.9—10.4 6H, 12.79 s, 14.04 s), show the structure to be X.

Hydrolysis of 1,2: 3,4-O-isopropylidene L-*xylo*-3-hexulose (XI)[3b] yielded a syrupy sugar XII[9] $[\alpha]_D^{24}$ −23° (c=1, H_2O), PPC (*Rf*: A 0.50, B 0.33, C 0.26), which gave upon $NaBH_4$ reduction a mixture which could be regarded on GLC of TMS derivative as a mixture of glucitol and dulcitol. This sugar yielded DNO XIII, $C_{18}H_{18}O_{11}N_8$, mp 250°, UV λ_{max}^{EtOH} nm (log ε) 402 (4.73) and 432 (4.72), which gave a triacetate XIV, $C_{24}H_{24}O_{14}N_8$, mp 226°, whose spectra, UV $\lambda_{max}^{CHCl_3}$ nm (log ε) 392 (4.67) and 436 (4.67), NMR (DMSO-d_6, δ 1.78 s 3H, 2.01 s 3H, 2.19 s 3H, 2.39 s 3H, 4.36 oct 2H, 5.58 m, 6.76 d, 7.9—9.0 6H, 11.25 s, 12.53 s) indicate the structure to be XIV. The chelate ring formation between the two 2,4-dinitrophenylhydrazine moieties[2] is also observed in the NMR spectra of X and XIV.

These 1-deoxy (2,4-dinitrophenyl)osazones would have been formed like 1-deoxycoriose (2,4-dinitrophenyl)osazone,[2] *via* 1-deoxyosones, XV, XVI and XVII, as the solution resulted by treating XII with warm 2N HCl for 1 hr and cooling to the room temperature, gave the precipitate of XIII immediately upon addition of the cold reagent solution, while XIII was not obtained when the reagent solution was added to XII without the previous treatment with 2N HCl.

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8) J.A. Cifonelli and F. Smith, *Anal. Chem.*, **26**, 1132 (1954).
9) Fragmentations of the TMS derivatives were presented at the 8th Symposium of the Mass Spectrometry of Organic Compounds, Hiroshima, Oct. 1973, and at the Annual Meeting of the Chugoku-Shikoku Branch of the Pharmaceutical Society of Japan, Matsuyama, Nov., 1973.