COMMUNICATIONS TO THE EDITOR

3-DEOXYHEXOSONES

Sir:

The 3-deoxyhexosones are accepted as intermediates in the conversion of sugars by alkali to metasaccharinic acids,[1] and also have been postulated as intermediates in the acid catalyzed production of furfurals from sugars.[2] Yet only the first member of the series, 2-oxopropanal, was known. The two possible 3-deoxy-D-hexosones now have been prepared and their behavior studied under alkaline and acid conditions.

Di-D-fructose-glycine[3] dihydrate[4] (Ia) was heated at 100° for 4.5 minutes in dilute aqueous solution at *p*H 5. Decationization and concentration yielded 3-deoxy-D-*erythro*hexosone (IIIa) as a colorless amorphous solid. Traces of impurities (less than 10%), which included glucose (1–2%) and mannose (1–2%) were removed by chromatography on a paper column giving the pure osone [Found: C, 44.53; H, 6.59]. Di-D-tagatose-glycine[4] (Ib) similarly gave 3-deoxy-D-*threo*hexosone (IIIb). Both osones readily gave osazones (Table I) in the absence of acid.

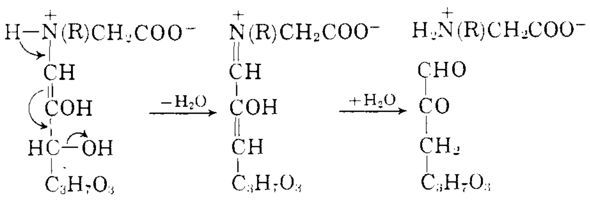
TABLE I

SUBSTITUTED PHENYLOSAZONES OF 3-DEOXYHEXOSONES[a]

Osone	Substituent	M.p., °C. (dec.)	$[\alpha]^{25}\text{D}$
D-*erythro*-	2,4-Dinitro-[b]	266	$+800^{\circ c}$
	Triacetate	184	$+588^{\circ d}$
	2,5-Dichloro-	242	$+400^{\circ e}$
	Triacetate	184	.....
	4-Nitro-[b]	260–262	$+350^{\circ c}$
D-*threo*	2,4-Dinitro-	258–259	$-500^{\circ c}$
	Tri-acetate	209	.....
	2,5-Dichloro	225	$-208^{\circ e}$

[a] All were crystalline and gave satisfactory analyses. [b] Identical with the corresponding osazone from 3-deoxy-D-glucose.[5] [c] Pyridine–acetic acid 1:1. [d] Chloroform. [e] Pyridine.

The formation of a 3-deoxyosone and the Lobry de Bruyn–Alberda van Ekenstein transformation are considered to proceed through a common intermediate, the 1,2-enediol of the sugar.[1] Dehydration of the sugar 1,2-enediol to the 3-deoxyosone is normally a side reaction,[1] but in the case of the diketose-amines the position is reversed and only traces of the epimeric aldoses are formed



I (Enol form) II III

Acids quantitatively converted 3-deoxyhexosones to 5-(hydroxymethyl)-2-furaldehyde ($\lambda_{\max}$ 284 mμ), 2,4-dinitrophenylhydrazone, m.p. 203°. The yields after heating for 2 hours at 100° in 2 *N* acetic acid were 45, 80, and 0.5% from IIIa, IIIb, and fructose, respectively. Alkali converted the 3-deoxyhexosones by an internal reaction of the Cannizzaro type to a mixture of the corresponding metasaccharinic acids. Paper chromatography of the lactones showed only "α-" and "β"-metasaccharinic lactones. The yield of glucometasaccharinic acids[6] from IIIa was 25% after only 5 minutes of standing at 25° in oxygen-free 0.038 *N* lime water. The "β" isomer was isolated as its calcium salt $[\alpha]^{25}\text{D}$ + 22° (*cf.* Nef[7]).

Because the 3-deoxyhexosones are converted rapidly by weak acid and alkali to 5-(hydroxymethyl)-2-furaldehyde and metasaccharinic acids, respectively, and because they give intense browning with amino acids,[8] these highly reactive substances may be significant intermediates in various types of sugar degradations.

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[1] J. C. Speck, Jr., *Advances in Carbohydrate Chem.*, **13**, 63 (1958).

[2] M. L. Wolfrom, R. D. Schuetz and L. F. Cavalieri, THIS JOURNAL, **70**, 514 (1948).

[3] 1,1′-(Carboxymethylimino)-bis-[1-deoxy-D-fructose].

[4] E. F. L. J. Anet, *Aust. J. Chem.*, **12**, 280 (1959).

[5] E. F. L. J. Anet, unpublished results.

[6] W. M. Corbett and J. Kenner, *J. Chem. Soc.*, 1431 (1955).

[7] J. U. Nef, *Ann. Chem. Liebigs*, **376**, 1 (1910).

[8] E. F. L. J. Anet, *Aust. J. Chem.*, **12**, 491 (1959).

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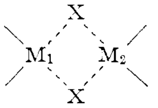
RECEIVED FEBRUARY 8, 1960

TRANSITION METAL CATALYSTS. III. NATURE OF THE ACTIVE SITE IN ORGANOMETALLIC CATALYSTS

Sir:

There is considerable interest in defining the active species in olefin polymerization catalysts formed from an organometallic reducing agent and a transition metal compound. Since two different compounds are employed and the compounds are usually electron deficient molecules, earlier investigators postulated, and later isolated, bimolecular coördination complexes having the halogen bridge structure[1,2,3]



M_1 = Electropositive metal from organometallic reducing agent such as aluminum.

M_2 = Transition metal of Groups IV-VI of the Periodic Chart (Ti, V, Cr).

Regardless of whether such complexes are essential or not, there is the separate problem of which metal is the site of chain propagation. Our copolymerization studies are pertinent to this problem.

Ethylene and propylene were copolymerized in cyclohexane using a 2-l., vigorously stirred autoclave[4] at 30 p.s.i. and 70°. Catalyst was injected

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[1] G. Natta, P. Pino, G. Mazzanti, E. Mantica and M. Peraldo, *J. Polymer Sci.*, **26**, 120 (1957).

[2] G. Natta, P. Corradini and I. W. Bassi, THIS JOURNAL, **80**, 755 (1958).

[3] W. L. Carrick, *ibid.*, **80**, 6455 (1958).

[4] J. D. Sutherland and J. P. McKenzie, *Ind. Eng. Chem.*, **48**, 17 (1956).