

Fig. 1. Structure of the cation $[O(HgI)_2HgOH]^+$; bond lengths [pm] and bond angles [°].

planar bis(iodomercurio)hydroxomercuriooxonium ions $[O(HgI)_2HgOH]^+$ (Fig. 1) and ClO_4^- ions occur in the lattice. To our knowledge this is the first example of a mononuclear metallo complex with an inhomogeneous second sphere to be discovered.

Deviations of the heavy atom skeleton from C_{2v} symmetry are due to varyingly strong additional interactions between ClO_4^- ions and the Hg atoms of the cation; intermolecular contacts perturbing the symmetry also exist between I and Hg atoms.

The mean distance between three-coordinate oxygen and mercury $\bar{R}(O-Hg) = 205$ pm agrees with the bond lengths in $[O(HgCl)_3]^+$ ($R(O-Hg) = 205$ pm)^[5]. The two equal bond lengths $R(Hg-I) = 257$ pm are significantly shorter than the corresponding values in the yellow modification of HgI_2 ($R(Hg-I) = 261$ pm)^[6]. This effect is attributable to the formal positive charge on the central oxygen atom. Similar short bond lengths between Hg(1) and the hydroxy-oxygen O(2) ($R(Hg-O) = 198(3)$ pm; Fig. 1) are known only for Na_2HgO_2 ($R(Hg-O) = 196$ pm; standard deviation not reported)^[7].

The occurrence of a hydroxyl group, whose proton could not be localized by X-ray study, and which is coordinated in such an unusual way to mercury, and also the formation of weak hydrogen bonds to ClO_4^- ions, were shown by vibrational spectrometry. Vibrational spectra of the isotopic tetrafluoroborate, $[O(HgI)_2HgOH]BF_4$, prepared analogously, show that the hydrogen bonds between the complex cations and the anions are even weaker in the latter, although the spectra are otherwise in full agreement.

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 $[O(HgI)_2HgOH]ClO_4$: 52165-26-1

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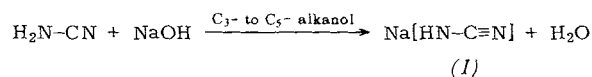
Improved Preparation of Monosodium Cyanamide

By Stefan Weiss and Helmut Krommer^[*]

According to an almost hundred years old process, monosodium cyanamide (sodium hydrogencyanamide) (1) which is

[*] Dr. S. Weiss and H. Krommer
Forschungsabteilung
Süddeutsche Kalkstickstoff-Werke AG
8223 Trostberg, Postfach 1150/1160 (Germany)

of interest as a starting material for syntheses can be obtained by treating cyanamide with sodium ethanolate in anhydrous ethanol^[1]. In a search for an industrially useful method of preparation we have found that cyanamide reacts smoothly at room temperature with sodium hydroxide in an alcoholic suspension, yielding exclusively (1) if the reaction medium is an aliphatic alcohol containing three to five C atoms^[2]. It is particularly significant that this method affords pure monosodium cyanamide in quantitative yield.



Experimental:

Finely powdered sodium hydroxide (80.0 g, 2.00 mol) is added with vigorous stirring to a solution of cyanamide (84.1 g, 2.00 mol) in 2-propanol (500 ml) while the temperature is kept at 25°C by cooling. After ca. 3 h a colorless, loose powder, sensitive to moisture, can be isolated by filtration and drying in a vacuum (40–50°C): 127 g (99%) of pure (1), characterized by elemental analysis and argentometric cyanamide determination.

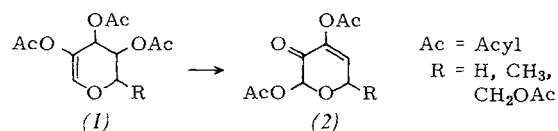
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Efficient Synthesis of Sugar 3,2-Enolones^[1] from 2-Hydroxyglycals and Their Conversion into 4-Pyrones

By Eleonore Fischer and Frieder W. Lichtenthaler^[*]

Although previously^[2] formulated as hypothetical intermediates in the long known conversion of acylated 2-alduloses into kojic acid derivatives^[3], sugar 3,2-enolones^[1] of type (2) have hitherto been obtained only from hexoses in the form of 1-O-methyl derivatives^[4], and then always by oxidation of difficultly accessible, partially acylated hexosides with subsequent β -elimination. We now describe an efficient synthesis of 1-acylated 3,2-enolones from 2-hydroxyglycyl esters (1) \rightarrow (2), which is applicable to hexoses, deoxyhexoses, and pentoses and via the 1-halo compounds, also provides ready access to the 1-alkoxy derivatives.



The chlorides (4)^[6] which are the primary addition products of chlorine^[5] to the perbenzoyl-2-hydroxyglycals (3a)–(3c) are stable only at low temperature and are extremely sensitive to hydrolysis. In the presence of water the tetrabenzoyl-2-aldulose (6a) or the tribenzoyl derivatives (6b) and (6c) are obtained, a finding which is readily interpreted by formation of the partially esterified orthoacid derivatives (5) and their decomposition. If, however, a benzene solution of (4) is heated for a short time in the presence of an acid-acceptor (e.g. aqueous $NaHCO_3$), hydrolysis to (6) is accompanied by elimination of benzoic acid with formation of the 3,2-enolones (7a)–(7c) in yields of 50–60% [based on (3a)–(3c)] (see Table 1).

Subsequent reactions of these benzoyl enolones were investigated mainly for the hexose derivative (7a). With HCl/acetyl

[*] Dipl.-Chem. E. Fischer and Prof. Dr. F. W. Lichtenthaler
Institut für Organische Chemie der Technischen Hochschule
61 Darmstadt, Schlossgartenstrasse 2 (Germany)