

After allowing to stand for four hours with occasional shaking, the paste was extracted with ether and the latter solution neutralized with solid potassium carbonate, filtered and evaporated in a vacuum. The residue was a small quantity of colorless sirup which crystallized after remaining in a vacuum for several weeks. After crystals were once obtained the sirups were readily crystallized by "seeding." Recrystallization from a mixture of ether and ligroin gave pure ethylidene α -methyl glucose, m. p. 77°.

Summary

1. The synthesis of hydroxypropyl vinyl ether and its methylated derivative is described.

2. The former compound, in contact with a trace of concentrated acid, is shown to rearrange quantitatively into the cyclic acetal, ethylidene trimethylene glycol.

3. Further evidence is brought forward regarding the mechanism of acetal, glucoside and polysaccharide formation, as well as the mechanism of the hydrolysis of this class of compounds.

4. This evidence supports the hypothesis of vinyl derivatives being the intermediates through which transformations of this nature take place.

MONTREAL, CANADA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF COLORADO] DIHYDROXY- AND DICHLORO-KETO-HEXAHYDROTRIAZINES

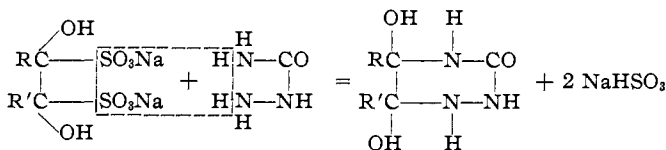
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Glyoxal and semicarbazide hydrochloride yield a mono-¹ and a disemicarbazone.² Similarly the aliphatic 1,2-diketones yield disemicarbazones,³ but not the mono-derivative. Aromatic diketones also yield semicarbazones in alkaline solution,⁴ but in acid solution the monosemicarbazones condense to triazine derivatives.³

If, on the other hand, semicarbazide hydrochloride and the sodium bisulfite addition products of glyoxal, methyl glyoxal or of aliphatic 1, 2-diketones are brought together in molecular proportions in hot water solution, there is a quantitative precipitation of a dihydroxy-keto-hexahydro- α -triazine, the compound being formed by a reaction accompanied by the splitting off of two moles of sodium bisulfite.



¹ O. Diels, *Ber.*, **35**, 347 (1902).

² Harries and Temme, *Ber.*, **40**, 171 (1907).

³ Posner, *Ber.*, **34**, 3977 (1901).

⁴ Thiele and Stange, *Ann.*, **283**, 6, 27 (1894); Biltz and Arnd, *Ber.*, **35**, 346 (1902).

The triazine derivatives thus obtained are insoluble in organic solvents except hot glacial acetic acid, in which they are slightly soluble and from which in very dilute solutions they may be obtained as minute colorless needles. They do not melt, but begin to decompose at definite temperatures. They are decomposed on boiling with strong acids, but in the cold yield salts. They are stable against hot alkalies. The two hydroxyl groups are replaced by chlorine on treatment with phosphorus trichloride, except in the case of the higher members which are decomposed by this reagent.

Experimental

I. Sodium Bisulfite Addition Products of Aliphatic 1,2-Diketones.—

We find no statement in the literature concerning these. When 1 mole of aliphatic 1,2-diketone is treated with 2 moles of sodium bisulfite in water solution, the diketone goes into solution and the yellow color disappears. By evaporating the solution, the crystalline addition product is obtained. The diketones were prepared from the corresponding mono-ketones by hydrolysis of the oximes prepared by means of nitrous acid.

TABLE I
SODIUM BISULFITE ADDITION PRODUCTS

Ketone	Decompn. temp., °C.	S, calcd., %	S, found, %
Diacetyl.....	145-155	21.77	21.21
Propionylacetyl.....	135-150	20.77	20.62
Butyrylacetyl.....	130-140	19.87	19.97
Valerylacetyl.....	100-110	19.04	19.27
Caproylacetyl.....	95-100	18.82	18.56

2. Dihydroxy-keto-hexahydro- α -triazines from Semicarbazide Hydrochloride and Sodium Bisulfite Addition Products of 1,2-Diketones.—The decomposition temperatures, formulas and analytical data of the triazines prepared are given in Table II.

TABLE II
DIHYDROXY-KETO-HEXAHYDRO- α -TRIAZINE AND HOMOLOGS

Derivative	Decompn. temp., °C.	Formula	Carbon, %		Hydrogen, %		Nitrogen, %	
			Calcd.	Found	Calcd.	Found	Calcd.	Found
.....	265-270	C ₃ H ₇ N ₃ O ₃	27.06	26.84	5.26	5.43	31.57	31.56
				27.27		5.50		
Methyl.....	250-255	C ₄ H ₉ N ₃ O ₃	32.65	32.34	6.21	6.20	28.57	28.40
Dimethyl.....	240-245	C ₅ H ₁₁ N ₃ O ₃	37.26	37.04	6.83	6.75	26.08	26.00
Methylethyl.....	230-235	C ₆ H ₁₃ N ₃ O ₃	41.14	41.27	7.42	7.38	24.00	24.12
Methylpropyl.....	240-245	C ₇ H ₁₅ N ₃ O ₃	44.44	44.49	7.93	7.66	22.22	22.05
				44.60				21.90
Methylbutyl.....	230-235	C ₈ H ₁₇ N ₃ O ₃	47.29	47.10	8.37	8.10	20.69	20.51
				47.01		8.37		20.52
Methylamyl.....	100-105	C ₉ H ₁₉ N ₃ O ₃	49.77	49.37	8.75	8.97	19.35	19.50
				49.68		9.04		19.60

3. **Dichloro-keto-hexahydro- α -triazines from Phosphorus Trichloride and the Compounds in 2.**—The decomposition temperatures, formulas and analytical data of these triazines are summarized in Table III.

TABLE III

Derivative	Decompn. temp., °C.	Formula	Carbon, %		Hydrogen, %		Nitrogen, %		Chlorine, %	
			Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
...	265-270	C ₃ H ₂ N ₃ OCl ₂	21.18	21.20	2.94	3.21	24.71	25.00	41.15	41.00
Methyl	260-270	C ₄ H ₇ N ₃ OCl ₂	26.08	26.00	3.80	3.80	22.82	22.83	38.58	38.56
Dimethyl	250-260	C ₅ H ₈ N ₃ OCl ₂	30.31	30.30	4.54	4.54	21.20	21.32	35.85	35.75
Methylethyl	240-245	C ₆ H ₁₁ N ₃ OCl ₂	33.50	33.41	5.19	5.30	19.81	19.60	33.65	33.50
				33.20		5.10		19.62		33.46
Methylpropyl	230-235	C ₇ H ₁₃ N ₃ OCl ₂	37.18	37.10	5.75	5.80	18.59	18.40	31.39	31.46

Experiments carried out with *isobutyryl*acetyl did not yield the expected dihydroxytriazine derivative. A soluble compound was formed whose constitution we have not yet determined.

Summary

1. Semicarbazide hydrochloride reacts with the sodium bisulfite addition products of glyoxal, methylglyoxal and 1,2-aliphatic diketones with the formation of dihydroxy-keto-hexahydro- α -triazines, compounds insoluble in the usual organic solvents except acetic acid, in which they are slightly soluble. They do not melt, but begin to decompose at definite temperatures; soluble in acids; stable against alkalis.

2. The above compounds yield with phosphorus trichloride dichloro-keto-hexahydrotriazines which resemble the original substances in their properties.

3. The sodium bisulfite addition products of a number of 1,2-diketones have been prepared.

BOULDER, COLORADO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF KANSAS] THE REDUCTION OF AROMATIC NITRO COMPOUNDS WITH SODIUM ALCOHOLATES

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Nearly 100 years ago (1834) Mitscherlich² used a solution of potassium hydroxide in ethyl alcohol as a reducing agent and obtained with nitrobenzene, azoxybenzene and the potassium salt of an organic acid. Since that time investigations in this field have been confined mainly to the action of various aromatic nitro compounds upon solutions of sodium in

¹ From a dissertation presented by C. M. Suter to the Faculty of the Graduate School of the University of Kansas in partial fulfilment of the requirement for the degree of Doctor of Philosophy.

² Mitscherlich, *Ann.*, **12**, 311 (1834).